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A SHORT HISTORY OF PHYSICS

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TO
P. J. B.

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PREFACE

THIS book is an attempt to give in a simple and concise manner an historical account of the development of physical science from its earliest origins to the present day. For unknown reasons histories of science do not appear to have been popular in the past if one may judge from the relatively very small number of such works in comparison with the histories of almost all other departments of knowledge. And yet it seems to the author that for the general reader, or for the specialist in one branch of science who is the general reader in another, the historical method is usually more interesting than, and has many advantages over, the more formal and logical method by which the majority of the present generation received their instruction in the exact sciences. Indeed their very exactness has probably been largely responsible for the adoption of the formal method, so that teaching by experimental demonstration followed by logical treatment (as opposed to psychological or historical treatment) has been general.

Concerning the advantages of the historical method, Clerk Maxwell observes in the preface to his *Treatise on Electricity and Magnetism* that "It is of great advantage to the student of any subject to read the original memoirs on that subject, for science is always most completely assimilated when it is in the nascent state." Ultimately of course for the serious student the purely systematic method becomes the only profitable one.

The historical aspect naturally brings one to the

consideration of the classics of scientific literature. It has been most surprising to the author to find how few specialists in various branches of physics were acquainted with even extracts from the masterpieces of Newton, Galileo, Boyle and Faraday, or had even handled the original memoirs to which at some period they had access in their University libraries. Admittedly the difficulty of obtaining reprints of many of the scientific classics is almost as great as that of securing the originals and one's only hope is the antiquarian book shop. The position does not seem to be quite so difficult now as it was a few years ago, for since this book was planned, Messrs. G. Bell & Sons have published the first numbers of a collection of the *Classics of Scientific Method*, while Messrs. Gauthier-Villars have produced a series of reprints entitled *Les Maîtres de la Pensée Scientifique*. In addition the Cambridge University Press has published *Cambridge Readings in the Literature of Science*, arranged by Mr. W. C. D. Whetham and his daughter. In German there has been available for a long time the excellent series of Ostwald's *Klassiker der Exacten Wissenschaften*.

Considerations such as the above have determined the form of this book in which the object has been to present the theories of modern physics as illustrative of scientific thought and as essentially developments from the successes and failures of earlier investigators, for only very rarely have they "leaped full grown and full armed from the brain" of any one worker. To do this in the space of a small volume has entailed the omission of much which some might regard as essential, and suppression of detail in order that a view of the whole might be obtained. In spite of this it is hoped that the picture presented is fairly complete, and that in the attachment of credit to individuals, a thorny problem at certain points, no great injustices have been committed.

With regard to the quotations throughout the book

which have been selected to give the opinions and speculations of the foremost investigators in their own words wherever such procedure has been thought useful, no claim is made that they have all been taken from the original memoirs, though this is true of the greater number. For much of his subject matter the author has used the works quoted at the ends of the chapters, and he gladly acknowledges his indebtedness to their authors.

He also wishes to express his thanks for helpful suggestions to Mr. F. H. Schofield, who read through the manuscript, and to Dr. J. S. Anderson and Mr. W. Barnett, who each read several chapters. His thanks are also due to Dr. J. W. T. Walsh, who cheerfully undertook the task of correcting the proofs.

H. B.

HAMPTON-ON-THAMES,
25th January, 1927

PREFACE TO SECOND EDITION

A FEW minor corrections have been made but otherwise this edition is the same as the first (1927).

During the past few years a considerable number of papers have been published in connexion with the further development of the general theory of relativity and also with the extension of the quantum theory in terms of what is called the wave mechanics or the new quantum mechanics. The contributions of Eddington, Einstein, Heisenberg, Schrödinger, Dirac, Jordan and others to these subjects, while of the greatest interest and importance, cannot be said as yet to have resolved our present grave difficulties and uncertainties. Whether they will do so is of course an open question, but it is thought that discussion of their work can scarcely be profitable at this stage in a book of this character.

H. B.

HAMPTON-ON-THAMES,
21st August, 1929

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A SHORT HISTORY OF PHYSICS

CHAPTER I

INTRODUCTORY

IN considering the origins of the various sections of that branch of Science usually referred to as Physics, we shall find that very often our earliest authorities are the Greek philosophers of the fourth and fifth centuries before the Christian era. Although these origins can be traced back to such a remote period, it is a striking fact that nearly all subsequent progress has been the result of the labours of the last three centuries. The interval between, though very largely devoid of important contributions to our knowledge of the laws of Nature, has, however, been productive of very many works of genius—literary, philosophical and artistic, so that in seeking the cause of this great hiatus in scientific progress we cannot ascribe it to any cessation of intellectual effort. It is true that certain periods in the history of Western Europe have been characterised as “dark ages,” but further examination discloses that these dark ages, though relatively unproductive of intellectual monuments, showed marked progress in the foundation and development of our modern economic and political systems.

A comparison of the methods and ideals of ancient and modern science does, however, afford an explanation of this slow progress, and shows very clearly that it is almost entirely due to the different points of view prevalent in the respective periods. We shall therefore in this chapter indicate wherein these differences lie, and trace the development of the modern spirit which has in so short a space of time enabled the human race to acquire an ever-increasing knowledge and control over the forces of Nature constituting its environment, and which promises to increase that knowledge in the future to an extent which it is impossible to limit.

From the earliest times of which we have record, man has indulged in speculation concerning the nature and causes of the many phenomena which the universe presents to him. In those very far-off days, in attempting explanations of his surroundings he almost invariably adopted an animistic view ;—thus, the sun was regarded as the chariot of the sun god—the rainbow, a bridge to Valhalla—thunder, the manifestation of the anger of Jove, and so on. In the works of various Greek philosophers of the fourth and fifth centuries before the Christian era, we are presented with the first attempts at natural explanations of these phenomena, or explanations in which complicated events are deemed referable to simpler specific properties of objects without the invocation of supernatural agencies.

The movements of the heavenly bodies provided a series of phenomena which were the object of much attention by the ancients. The regularity of their motions was early recognised, and important astronomical periods (e.g. the length of the year, the Saros cycle, the obliquity of the ecliptic and of the moon's orbit, etc.) were determined, though it was considered that the earth was at the centre of the universe and that the sun and the stars revolved round it. Later, Aristarchus (310-230 B.C.) put forward a heliocentric theory of the solar system.

The problem of matter was also the subject of much speculation. Its metamorphoses in the animal and vegetable kingdoms suggested that matter might ultimately consist of a single primordial substance, or at any rate of a few substances. Empedocles (494-434 B.C.) claimed that earth, water, air and fire were the ultimate constituents of all forms of matter, which he supposed owed their differences in properties to the various proportions of these elements contained in them. Leucippus (*circa* 500 B.C.) and Democritus (465-375 B.C.) brought forward a theory of atoms, in which different portions of matter were considered to owe their properties to differences in motion and arrangement of ultimate atoms, all of the same nature, of which they were composed.

These and other theories were developed, but no methods of testing them were open to their adherents, so that in reality they were no more than opinions, though of value

inasmuch as they tended to emphasise the idea that the phenomena of the universe obeyed definite laws and were capable of natural explanations.

Many other interesting speculations date from this period, which was particularly rich in "natural philosophers." Mathematics, too, made rapid progress about this time, geometry, for instance, reaching a high degree of excellence. Pythagoras (572-497 B.C.) following Thales (*circa* 640-548 B.C.) laid the foundations of Greek geometry. His most famous proposition was, of course, the theorem that in a right-angled triangle the square on the hypotenuse is equal to the sum of the squares on the other two sides. He is also supposed to have developed the theory of proportionals. His followers—the Pythagoreans, seem to have been familiar with what is covered by Books I, II, IV and VI of Euclid (*circa* third century B.C.), and probably most of Book III. Incommensurable lines or irrationals were discovered, and the theory of proportion was extended to deal with incommensurable as well as commensurable magnitudes. Accompanying the progress of geometry was the growth of the abstract sciences of politics, ethics and logic. These branches of learning were developed to an extraordinary extent by the philosophers of the "golden age" at Athens, and strange as it may at first appear it was probably due to this excellence that the growth of natural science, which was promising to be very great, suffered a serious check.

For none of these sciences, however far they are developed, need correspond with reality. It is sufficient for them all if they are self-consistent. Geometry, for example, makes use of certain fundamental notions which we all possess regarding space, and from the assumption of these, deduces a vast superstructure which is entirely self-consistent and independent of the actual existence of the straight lines, triangles and circles with which it is concerned. Similarly, ethics is concerned with the study of behaviour deduced from certain fundamental axioms. Now the results obtained by geometry carried universal conviction because its axioms received universal consent, but no such agreement was possible in the case of natural philosophy, politics, ethics or logic. Hence, in all these branches of science, each philosopher created his own system and maintained

it in disputation to the best of his ability, so that in the multiplicity of systems true science almost disappeared.

The greatest philosophers of this period were Plato and Aristotle.

Plato (*circa* 427-347 B.C.) was the exponent of the Deductive Method of gaining knowledge. He held that all knowledge was merely the recollection of experiences in previous existences. This idea seems to date back very much before Plato as it was part of the ancient Hindu doctrine of Krishna that "truth was originally implanted in mankind, but having been suffered gradually to slumber, it was finally forgotten. Since that period knowledge returns as a recollection." In consequence he was not so much concerned with facts as with his own conceptions. In Plato's philosophy sound conclusions were arrived at by reference to the opinions of the majority, or of those who were supposed to be learned. From these "authoritative" opinions as axioms he would then deduce by a logical process, universal truths which he would support with those facts of experience with which they accorded, those with which they were at variance being often ignored. Plato regarded the inner consciousness, or the Intellect as the source of knowledge, so that his philosophy tended to be wholly introspective.

Aristotle (384-322 B.C.), who was a pupil of Plato, believed that knowledge was gained by remembering, classifying and comparing numerous particular events and that as a result the mind was led to make an *induction* as to their cause or nature. He recognised that from the induction, deductions could be made, which should, however, be tested to see if they agreed with experience. He realised the great possibility of error in Plato's system, as deduction is only sound when based on established facts, not on the tenets of the "wise." Thus Aristotle regarded Experience as the source of knowledge. Aristotle presented his scientific method in the *Organon* (i.e. Instrument), a collection of six of his logical treatises, in which he showed how from facts truly ascertained, scientific laws can be established and that new truths can then be deduced by the method of Plato.

The following quotations from various of his works indicate clearly the importance which Aristotle attached

to experience in science. "Let us first understand the facts, and then we may seek for the cause." "From sense, therefore, as we say, memory is produced, but from repeated remembrance of the same thing, we get experience, for many remembrances constitute one experience." "Without sensation thought is impossible. It is from sense that we gain knowledge of particulars (i.e. facts). It is from induction that we gain knowledge of universals (i.e. laws), and these can be reached only through experience."

In addition to the exposition of the method by which knowledge should be acquired, Aristotle applied it himself to a certain extent and produced numerous works in almost every department of knowledge. Thus in order to write his *Natural History* he had specimens of plants and animals collected from all parts of the then known world, so that he could write down his facts from actual observation. In Botany, Zoology, Art, Poetry, Ethics and Politics, he was responsible for works and ideas which are justly regarded as being of great importance in the history of civilisation, while he discussed with a sagacity far surpassing that of any other writer, the problems of Meteorology, Mechanics, Astronomy, Chemistry, Geology, etc.

As regards his Physics, however, Aristotle was in many cases by no means a faithful follower of his own doctrines, as he himself fell a victim to preconceived notions, while he could not at times prevent metaphysical considerations regarding truth, reality and existence from invading his scientific arguments.

Two of the errors into which he fell are deserving of consideration, since they later proved very serious stumbling-blocks in the path of science. One of these arose in connection with the atomic theory, which he dismissed very largely on metaphysical grounds. These led him to assert its impossibility and so caused the rejection of the theory even in his own time. The atomists asserted that since all bodies were composed of the same elementary atoms they would all fall at the same rate in a vacuum, —a conclusion quite correct though not founded on correct reasoning. Aristotle agreed to this proposition, but the observed fact that they did not do so led him to deny the possibility of the existence of a vacuum and hence to the

assertion that "nature abhors a vacuum," a principle which played an important part in the dialectics of the Middle Ages. The differences in the actual motions of bodies he referred to their natural tendencies—light bodies, upwards, and heavy bodies, downwards, each seeking its proper place in the universe; whilst the qualities of hardness, colour, etc., he considered as inherent properties which must be taken as axiomatic, and into which it was futile to enquire further. Similarly, his speculations regarding the movements of the stars and planets led him to propound ideas regarding motion which held back the progress of dynamics for centuries. In particular he argued that motion in a circle was the most natural motion for a body, since the circle was considered to be the perfect curve.

Herschel in his *Natural Philosophy*, quoting from Galileo's attack on the Aristotelian doctrines in the *System of the World*, gives the following as an example of the argument to prove that the heavens are immutable, incorruptible and eternal:—

I. Mutation is either generation or corruption.

II. Generation and corruption only happen between contraries.

III. The motions of contraries are contrary.

IV. The celestial motions are circular.

V. Circular motions have no contraries.

Because there can be but three simple motions—

(1) To a centre.

(2) Round a centre.

(3) From a centre.

Of three things only one can be contrary to one. But a motion to a centre is manifestly the contrary of motion from a centre.

Therefore a motion round a centre (i.e. circular motion) remains without a contrary.

VI. Therefore celestial motions have no contraries—*therefore* among celestial *things* there are no contraries, *therefore* the heavens are eternal, immutable, incorruptible and so forth.

With arguments of this type it is possible to deduce any desired conclusion concerning any natural phenomenon.

A comparison of the methods of these two philosophers

affords a comparison of the difference in method to which we have already referred. Unfortunately the success of Aristotle's works and the recognition of his pre-eminence secured for him so great a reputation, that the rest of the civilised world for many centuries became slaves to his authority. Not only were the best and well-established portions of his works regarded as expressions of the eternal truth, but the many incorrect notions to which he gave the weight of his authority obtained a hold on the minds of men which it is difficult at the present day to imagine. In this connection, it is worthy of note that in the sixteenth century the citizens of Geneva passed the following resolution: "For once and for ever, in no branch of learning shall any one stray from the philosophy of Aristotle."

If the philosophers succeeding Aristotle had revered their illustrious predecessor by putting his precepts regarding experiment and observation into practice, instead of by merely accepting his system as the complete expression of truth, the development of science might have been very different from that which is presented to us in its history for almost 2000 years after his death.

Besides this neglect of the importance of observation and experiment in natural science there was, however, another great contributory reason for the absence of progress. This was the common ideal of the ancients that the function of knowledge was solely to elevate the mind, or as it was expressed "to form the soul, in the contemplation of eternal truth."

"The ancient philosophers," writes Macaulay in his Essay on Bacon, "did not neglect natural science; but they did not cultivate it for the purpose of increasing the power and ameliorating the condition of man. . . . Seneca wrote largely on natural philosophy, and magnified the importance of that study. But why? Not because it tended to assuage suffering, to multiply the conveniences of life, to extend the empire of man over the natural world; but solely because it tended to raise the mind above low cares, to separate it from the body, to exercise its subtilty in the solution of very obscure problems. Thus natural philosophy was considered in the light merely of a mental exercise. It was made subsidiary to disputation, and it consequently proved barren of useful discoveries."

Indeed, in the opinion of many philosophers, the production of anything useful would have been held to be degrading both to the philosopher and to philosophy. In particular, the science of mechanics was regarded as the least worthy of study. Seneca (3 B.C.-A.D. 65) is very insistent on this aspect of science as the following passage shows. "In my own time," he writes, "there have been inventions of this sort, transparent windows, tubes for diffusing warmth equally through all parts of a building, shorthand which has been carried to such a perfection that a writer can keep pace with the most rapid speaker. But the inventing of such things is drudgery for the lowest slaves; philosophy lies deeper. It is not her office to teach men how to use their hands. The object of her lessons is to form the soul. *Non est inquam, instrumentorum ad usus necessarios opifex.*"

With experimental science considered as a degrading occupation for a free man, is it to be wondered at that progress was small and that the ancients produced a philosophy merely of words and not of works?

After the fall of Athens from its political supremacy in 338 B.C., the centre of Greek culture moved to Alexandria, which, under the beneficent rule of the Ptolemies (324-43 B.C.), became the meeting place of philosophers from all parts of the world. The Alexandrian school produced many famous scholars, including Euclid (*circa* 300 B.C.), Aristarchus (310-230 B.C.), Apollonius (265-190 B.C.), Hipparchus (*circa* 150 B.C.) and later Ptolemy (A.D. 100-178). It was particularly rich in geometers and astronomers.

Alexandria in its turn fell in A.D. 640 to the Arabs who, after a brief period of conquest and destruction which carried them all over Northern Africa and Spain, assimilated the Greek learning, and at the end of the century became the sole guardians and teachers of the old philosophy. The rest of Europe, busy with the migrations of the Northern Peoples, found its whole activities bound up in the movements which have since led to its present political division, and for a time completely disappeared in what have been called the "dark ages."

Civilisation owes a great debt to the Arabs who at this troublous time in the history of Europe preserved and added very largely to the ancient knowledge. Whilst the rest of

Europe was, for the most part, in intellectual darkness, priest-ridden, and under the stifling influences of authority and intolerance, the Khalifate encouraged learning, exalted the supremacy of reasoning, founded important universities and libraries from Bagdad to Granada, and did everything possible to apply scientific knowledge to the purposes of everyday life, so much so that the Crusaders were astonished at the magnificence and splendour of the civilisation with which they were confronted. That the contributions of the Arabs to science were by no means slight is shown by the following words, all of Arabic origin—nadir, zenith, alchemy, alkali, alembic, alcohol, algebra, cipher, carat, elixir, which still possess their original significance.

Their foremost philosophers, Ben Musa (*circa* A.D. 800) in algebra, Alhazen (died, 1038) in physics, Geber (eighth or ninth century) in chemistry, Avicenna (980-1037) in medicine, Averroes (1126-1198) in medicine and philosophy, all left their respective branches of learning substantially enriched as a result of their labours, while it was to Averroes that the rest of Europe was indebted for its acquaintance with Aristotle. The Arabian universities also were the sources from which most of the great men of the early Middle Ages derived both their knowledge and inspiration. Adelard (12th century), Albertus Magnus (*circa* 1206-1280) and Roger Bacon (*circa* 1214-1294), all came into contact with the Arabian philosophy and drew from thence the ideas of free enquiry, of experiment and of reverence for learning, which characterised their lives.

The year 1492 witnessed the expulsion of the Arabs from Spain, and the extinction of that brilliant source of scholarship which had lasted so long. The effects of the Arabian learning remained, however, and in Roger Bacon we possess the connecting link between the Arabs and the Renaissance which was partly a result of the capture of Constantinople by the Turks in 1453, and the consequent re-discovery of the original Greek philosophy which the old quarrel between the Greek and Roman Churches had kept as the exclusive possession of Eastern Europe.

The scientific training which he acquired from the study of the Arabian commentators and philosophers inspired Bacon with a vehement distrust of the doctrines and teachers of his day. Aristotle was known only in fragmentary

portions chiefly through bad translations from the Arabic, as no one knew Greek, while physical science consisted in dialectics based on unsound premises resting solely on authority or custom. As a result he withdrew from the world and devoted himself to the study of languages and experimental science. His contributions to science are contained in the *Opus Majus*, *Opus Minus* and *Opus Tertium*, which he wrote in deference to the wishes of Pope Clement IV in spite of great opposition from his superiors in the Franciscan order.

He clearly recognised the interdependence of the sciences in the *Opus Tertium*, where he writes, "All sciences are connected together, and mutually assist one another, like members of the same body, each one of which performs its own function, not only for itself, but for all the others." He was also very clear in his ideas as to the origin of knowledge. "For we have, indeed," he explains in another place, "various means of knowing—authority, reasoning, experiment; but authority has no value unless it is accounted for; it does not enable one to understand, it only makes one believe; it imposes itself upon the mind without enlightening it. As to reasoning, sophistry cannot be distinguished from demonstration, except only by verifying the conclusion by experiment and practice." And again he writes, "There are two modes of investigation, viz. through argument and through experiment. Argument concludes and makes us conclude the question; but it does not certify. . . . For, if any man who has never seen fire has made it credible through sufficient arguments, that fire burns and harms, and even destroys things, the mind of the hearer would never on this account be still, and would not avoid fire before he has put his hand or anything combustible into fire, so that he would prove through experience what argument taught, but by the additional experience of combustion the mind is made certain, and finds rest in the brightness of truth—whence argument does not suffice, but experience does."

He also recognised the importance of mathematics in science, for he calls it the "alphabet of philosophy." "Physicists must understand," he writes, "that their science is powerless, if they do not apply to it the power of mathematics." While again we read, "Armed with ex-

periment and calculation, science must not be content with facts, though these may have their utility ; it seeks truth ; it wants to find out the laws, the causes—*canones, universales regulæ*."

Not only had Bacon such sound notions of the importance of experiment in science, but he practised his own doctrines, and, particularly in optics, made many important discoveries. It is not considered impossible by many that he actually invented the microscope and the telescope, for in the *Opus Majus*, after describing the effects of lenses, he states : " It is easy to conclude from the laws just spoken of that the largest things may appear small, and *vice versa* ; that remote objects may appear quite close, and reciprocally ; for we can cut glasses in such a manner, and adjust them in such a way as regards our eyesight and exterior objects, that the beams are broken and refracted in the direction we choose ; so that we shall see a close or remote object under whatever angle we please ; and thus at an incredible distance we should read the most minute letters, we could count the grains of sand and of dust, on account of the great width of the angle under which we should see them, for the distance by itself has no direct importance, but the size of the angle has."

Unfortunately Bacon was before his time, and his work did not receive the appreciation which a more enlightened age would have accorded it. The invention of printing was not destined to occur until many years after his death, so that the ideas embodied in the work of " this greatest apparition of the Middle Ages " did not bear fruit.

Still even apart from Bacon, other philosophers in time arose who recognised that progress was only to be made by direct appeal to Nature. Of these one of the most notable was the almost superhuman genius Leonardo da Vinci (1452-1519) who is responsible for the following prescient remarks : " In treating any particular subject, I would first of all make some experiments, because my design is first to refer to experiments and then to demonstrate why bodies are constrained to act in such a manner. This is the method we ought to follow in investigating the phenomena of Nature. Theory is the general, experiments are the soldiers. Experiment is the interpreter of the artifices of Nature. It is never wrong ; but our judgment is

sometimes deceived because we are expecting results which experiment refuses to give. We must consult experiment and vary the circumstances, till we have deduced general laws, for it alone can furnish us with them."

Others, too, who appealed at about this period to observation and experiment were Copernicus (1472-1543), Kepler (1571-1630), Gilbert (1544-1603) and Galileo (1564-1642), and the immediate result was in every case a great extension of real knowledge.

We must now consider the work of Francis Bacon (1561-1626) who has been accredited by many as the founder of modern science. His claim to this distinction rests on a series of philosophical works having for their object the reorganisation of the sciences and the development of a new method of learning, through which the mind, by means of rules and precepts, should automatically be enabled to make progress and discoveries in the various sciences. The most important of these works are the *De Augmentis Scientiarum* and the *Novum Organum*.

In direct opposition to the opinions of the Greek philosophers, Bacon maintained that the value of knowledge depended solely on its utility. It was due to his intense conviction that the knowledge man then possessed was of very little use that he was led to undertake the reorganisation of the sciences for the restoration of man to that command over Nature which he was supposed to have lost at the expulsion from Eden. "The knowledge whereof the world is now possessed," he affirms, "especially that of nature, extendeth not to magnitude and certainty of works." To Bacon the aim of science was not only to search for and to contemplate Truth, but "to endow the condition and life of man with new powers or works," and to "extend more widely the limits of the power and greatness of man."

The first portion of the *Instauratio Magna*, as the series is called, consists of a survey of the whole of the world's knowledge of science, together with an admirable classification of the sciences. After the survey comes the exposition of the method by which the human mind is to be trained in an infallible way to make progress and discovery. He realised that his method was quite new, and that the disciples of other methods would oppose it, so he first

disarms his opponents by subjecting them to destructive criticism. The Schoolmen, accepting the authority of Aristotle, and declaring that science was fully known and expounded in his works, are severely dealt with, as are those who constructed the universe from preconceived notions—*ex analogia hominis*, and also those who practised a blind empiricism—a groping in the dark.

Bacon devoted a considerable portion of the *Novum Organum* to the examination of the errors into which the mind is prone to fall and made suggestions for their avoidance. These “*Idola*” or false ways of looking at things he distinguished as (1) *Idola Tribus*—(Idols of the Tribe)—a tendency to ignore negative instances, and to generalise from insufficient data, (2) *Idola Specus*—(Idols of the Cave)—errors dependent on the constitution of the individual, which are to be avoided by viewing with suspicion “whatever the mind seizes and dwells upon with satisfaction,” (3) *Idola Fori*—(Idols of the Market Place)—errors arising from words and names which suggest relationships which are non-existent, and (4) *Idola Theatri*—(Idols of the Theatre)—errors arising from false philosophies.

As regards the method itself in its application to the study of phenomena, the first essential he states is to observe and collect the facts—what he calls “a natural history.” “First of all,” he writes in his *Novum Organum*, “we must prepare a *natural and experimental history*, sufficient and good; and this is the foundation of all.” Then by consideration of the facts, their rearrangement, and the comparison of the cases in which phenomena are present or absent or in which they are present in varying degrees, and the elimination of the non-essential features, the mind is led to make the induction which gives the true cause of the phenomenon in question. Such was the method of Bacon in which induction, controlled in the way he indicates, was the thread—the “*filum labyrinthi*.” “Then and only then may we hope well of the sciences, when in a just scale of ascent and by successive steps, not interrupted or broken, we rise from particulars (facts) to lesser axioms (laws); and then to middle axioms, one above the other; and last of all to the most general.”

Bacon’s method, however, which “nearly levels all wits and intellects,” is quite impracticable on account of its

cumbersomeness, and no evidence can be shown of its successful application in any branch of science. Bacon neglected the importance of the hypothesis or inspired guess which by suggesting possible explanations, even in the presence of but few facts, can be followed up, tested by experiment and its implications verified. The hypothesis, in not necessitating a complete natural and experimental history to suggest it, as would be required in Bacon's infallible process, anticipates and predicts the facts which the latter regards as being the foundation of all.

Though his system has not proved of the assistance he anticipated, nor are there any discoveries to which he can lay claim, Bacon really played a very important part in the history of science. This is because he expressed so well and so eloquently ideas which were, so to speak, waiting for expression at the time, and because above all he provided a *motive* for the study of science.

As we have seen, many of the ideas of Francis Bacon are met in the writings and works of the older Bacon, da Vinci and others. Bacon appeared at the right moment—the height of the Renaissance; scholasticism had begun to fall before the attacks of real enquirers, authority was being replaced by experiment all over Europe. Then Bacon came and expressed the spirit of the age in a series of epoch-making books which were received with so great admiration abroad that Voltaire hailed him as “le père de la philosophie expérimentale.”

It is at this period that modern science really begins. Herschel in his *Preliminary Discourse on the Study of Natural Philosophy* writes of the immediately succeeding years as follows: “The immediate followers of Bacon and Galileo ransacked all nature for new and surprising facts, with something of that craving for the marvellous, which might be regarded as a remnant of the age of alchemy and natural magic, but which under proper regulation is a most powerful stimulus to experimental enquiry. Boyle, in particular, seemed animated by an enthusiasm of ardour, which hurried him from subject to subject, and from experiment to experiment, without a moment's intermission, and with a sort of undistinguishing appetite, while Hooke (the great contemporary, and almost the worthy rival, of Newton) carried a keener eye of scrutinising reason into a

range of research even yet more extensive. As facts multiplied, leading phenomena became prominent, laws began to emerge, and generalisation to commence ; and so rapid was the career of discovery, so signal the triumph of the inductive philosophy, that a single generation and the efforts of a single mind sufficed for the establishment of the system of the universe, on a basis never after to be shaken."

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CHAPTER II

PLANETARY THEORY, MECHANICS AND THE LAWS OF MOTION

AMONG the subjects studied by the ancients that of astronomy is one whose origin can be traced back almost as far as the earliest times of which we have record. The connection between the positions of the celestial bodies and the seasons for sowing, reaping, and other occupations was very early realised, and used as a method of estimating time. Although the ancients possessed no observing instruments they acquired a very extensive knowledge of astronomical phenomena from naked eye observation. The Babylonian astronomers, for instance, were acquainted with several planets and had determined the interval between successive returns of the planets to the same places in the heavens. Thus they knew that Venus returned to a given starting-point in the sky in about eight years, and similar periods extending up to a period of eighty-three years had been determined for the other planets, while their observations on eclipses had resulted in the recognition of the Saros Cycle of 223 lunations, at the end of which the moon returns to the same position relative to the sun and to its own nodes and perigee. Lunar and solar eclipses were predicted with considerable accuracy, and astronomical almanacks were published.

Explanations of the apparent movements of the stars and other celestial bodies were early conceived, and it is to the consideration of certain of these theories that the earlier portions of this chapter will be devoted. Most of these theories referred the centre of the universe to the earth, round which the sun, moon, planets and stars were believed to revolve. This, of course, is the most

obvious interpretation of the apparent motions of these objects with reference to the earth.

Aristotle (384-322 B.C.) gave a summary of the astronomical theories of his time in one of his books. "Some say," he writes, "that the earth rests on water. We have ascertained that the oldest statement of this character is the one accredited to Thales the Milesian (624-547 B.C.), to the effect that it rests on water, floating like a piece of wood or something of that sort." He himself was of opinion that the earth was spherical and immovable, and that the paths of the various celestial objects round the earth were circular because motion in a circle was the most perfect kind of motion.

Pythagoras of Samos (572-497 B.C.) seems to have taught that the earth had a spherical shape and that it was poised in space. To him also is due the idea of the crystal spheres as the vehicles of the heavenly bodies and their attuning to divine harmonies resulting in "the music of the spheres."

The first to propose a heliocentric theory at all resembling our present idea was Aristarchus of Samos (310-230 B.C.). This was described by Archimedes in his *Arenarius*, but it met with no approval, and its author was accused of impiety as was Galileo in later years.

According to Archimedes, who was a younger contemporary of Aristarchus, "Aristarchus of Samos brought out a book consisting of some hypotheses, in which the premises lead to the conclusion that the universe is many times greater than that now so called. His hypotheses are that the fixed stars and the sun remain unmoved, that the earth revolves about the sun in the circumference of a circle, the sun lying in the centre of the orbit, and that the sphere of the fixed stars, situated about the same centre as the sun, is so great that the circle in which he supposes the earth to revolve bears such a ratio to the distance of the fixed stars as the centre of the sphere bears to its surface." This passage leaves no doubt that Aristarchus had in mind a very definite heliocentric theory similar to that proposed by Copernicus.

The Pythagoreans, according to Aristotle, were also responsible for a partial anticipation of the heliocentric theory in which the earth and the planets do not revolve

about the sun, but about an assumed central fire. The sun and moon were also supposed to take part in this motion together with a dark body—the counter-earth or “*antichthon*,” which was probably introduced into the theory to explain the frequency with which eclipses of the moon occurred.

Heraclides of Pontus (388-315 B.C.) discovered that Mercury and Venus revolved round the sun, and we are told that he “and Ecphantus the Pythagorean make the earth move, not in the sense of translation but by way of turning as on an axle, like a wheel, from west to east, about its own axis.”

Among the greatest astronomers of antiquity, Hipparchus and Ptolemy at Alexandria stand out far above the rest. Hipparchus (*circa* 150 B.C.) determined the chief astronomical data—the length of the sidereal year, the obliquity of the ecliptic and of the moon’s path and the eccentricity of the sun’s orbit with considerable accuracy. To him is due the idea of “eccentrics,” that is the displacement of the earth from the centre of the circles described by the sun and the moon. Ptolemy (A.D. 100-178), adopting very largely the theories of Hipparchus, extended them considerably, and drew up a system of astronomy in his book, the *Almagest*. The doctrine of an immovable earth was an essential feature of his system. It had been suggested that the earth had an axial motion, but he refused to countenance this idea. He further complicated the circular motions of the heavenly bodies by the introduction of epicycles. The *Almagest* represents the highest effort of the ancient astronomers, and after Ptolemy there arose no important contributors to astronomical science for several hundred years. In the meantime the authority of Ptolemy in astronomy became somewhat similar to that of Aristotle in the other branches of knowledge, so that the idea of questioning the Ptolemaic system hardly arose until the time of Copernicus.

However, in the later years of the fifteenth century we find the first results of the new spirit of enquiry which was to culminate in the Renaissance. Not only were the opinions of Aristotle subjected to investigation, but the Ptolemaic system began to receive its first serious criticism. As a result of his student days in Italy, Nicolaus Copernicus

(1473-1543), a Pole, came into contact with the revival of the Pythagorean theory which was then being discussed *sub rosa*. He was much impressed by the simplification which was introduced into the description of the planetary and solar motions, if they were referred to the sun as the centre of the universe. He laid the foundations of his heliocentric theory between 1506 and 1512, but deferred publication until 1543, when his *De Revolutionibus Orbium Cælestium* appeared.

The fundamental doctrines herein asserted were (1), that the apparent daily motion of the celestial sphere from east to west is due to the daily rotation of the earth on its axis from west to east; and (2), that the earth is one of a family of planets revolving round the sun. As an immediate result the motions of the sun and planets could be described without the use of the very large number of the epicycles and eccentrics which had from time to time been proposed to make the geocentric theory accord with the observed celestial motions. That all the epicycles did not disappear was due to the fact that Copernicus did not entirely free himself from the effect of the notions of the earlier philosophers, as he still believed in the old doctrine that "the movement of the heavenly bodies is uniform, circular, perpetual, or else compounded of circular movements."

Thus the new scheme was by no means perfect, so that Copernicus merely put forward his doctrine of the arrangement and motions of celestial bodies hesitatingly, and rather in the nature of a simplifying hypothesis. It was pointed out that in consequence of the assumed motion, the positions of the fixed stars should appear to vary and depend on the relative position of the sun and the earth, while Copernicus himself suggested that Mercury and Venus should exhibit phases similar to those presented by the moon, neither of which effects had been observed.

The following extract from his *De Revolutionibus* gives a description of Copernicus' idea of the universe: "First and above all," he states, "lies the sphere of the fixed stars, containing itself and all things, for that very reason immoveable; in truth the frame of the universe, to which the motion and position of all other stars are referred. Though some men think it to move in some way, we assign

another reason why it appears to do so in our theory of the movement of the earth. Of the moving bodies first comes Saturn, who completes his circuit in XXX years. After him, Jupiter, moving in a twelve year revolution. Then Mars, who revolves biennially. Fourth in order an annual cycle takes place, in which we have said is contained the earth, with the lunar orbit as an epicycle. In the fifth place Venus is carried round in nine months. Then Mercury holds the sixth place, circulating in the space of eighty days. In the middle of all dwells the sun. Who indeed in this most beautiful temple would place the torch in any other or better place than one whence it can illuminate the whole at the same time? Not ineptly, some call it the lamp of the universe, others its mind, others again its ruler—Trimegistus, the visible God, Sophocles' Electra the contemplation of all things. And thus rightly in as much as the Sun, sitting on a royal throne, governs the circumambient family of stars. . . . We find, therefore, under this orderly arrangement, a wonderful symmetry in the universe, and a definite relation of harmony in the motion and magnitude of the orbs, of a kind it is not possible to obtain in any other way."

The influence of the Church which regarded these views as contrary to its interpretation of the Bible, coupled with man's natural conservatism, prevented the acceptance, except by a few, of these new ideas. Among the many hostile critics Tycho Brahé (1546-1601), whose accurate observations were afterwards to do so much for the establishment of the theory, was pre-eminent. His objection to the Copernican theory was probably very much influenced by his failure to detect the change in position of the fixed stars due to the earth's motion round the sun. His opposition was not due to prejudice, however, as he was a most diligent observer, and for twenty-five years patiently measured and recorded the positions of the stars and planets with an accuracy little short of marvellous, so as "to lay a solid foundation for his views by actual observation, and then by ascending from these to strive to reach the causes of things." He suggested that the difficulties of Copernicus' system would disappear if the relative movements of the members were still maintained, but the earth itself regarded as immovable. In this form the theory is

very similar to that presented by Heraclides, in so far as the sun, earth, moon, Venus and Mercury are concerned.

The honour of placing the Copernican doctrines on a firm foundation, however, is to be ascribed to Johann Kepler (1571-1630). For a time he had been associated with Tycho Brahé, under whose direction he had been calculating the orbit of Mercury. In spite of this association, he was a firm believer in the Copernican system, and on the death of Tycho Brahé, he commenced a long series of calculations with the object of demonstrating the truth of the principles of the new system.

In the diligent and accurate observations of Brahé he found magnificent material for this work. The Copernican theory was sufficient to give a general description of the motions of the planets, but whenever tested by the results of observation on the planet Mars, there was always an error of eight or nine minutes of arc which could not be attributed to inaccuracy in Brahé's work. "Out of these eight minutes," writes Kepler, "we will construct a new theory that will explain the motions of all the planets."

He at first adhered to the theory of uniform motion in a circle, but observations of Mars (which showed great anomalies on account of the large eccentricity of the orbit) showed that this was not correct. Continuing the work, he then discovered that it moved in an ellipse, at one of the foci of which the sun was situated, whilst its velocity, instead of being constant, was such that the areas described in equal times by a line from the sun to the planet were equal. These statements, called Kepler's First and Second Laws, were published in 1609 in his commentary *De Motibus Stellæ Martis*, together with their application to the case of the earth and the other planets. The third of the so-called Kepler's Laws was announced ten years later in his *De Harmonica Mundi*. This Law is to the effect that "the proportion existing between the periodic times of any two planets is exactly the sesquiplicate proportion of the mean distances of the orbits," that is the squares of the periodic times are proportional to the cubes of the mean distances.

In the introduction to his *De Motibus Stellæ Martis* he endeavoured to account for the motions of the planets. The following passage shows that he had some idea of a

theory of gravitation, but it was so very much confused with notions about "virtues, animal forces, magnetic vortices," etc., that it is doubtful whether any credit can be claimed for him on this account. "If two stones were placed in any part of the world near each other, and beyond the influence of a third cognate body, these stones, like two magnetic needles, would come together in the intermediate point, each approaching the other by a space proportional to the comparative mass of the other. If the moon and earth were not retained in their orbits by their animal force or some other equivalent, the earth would mount to the moon by a fifty-fourth part of their distance, and the moon fall towards the earth through the other fifty-three parts, and they would there meet, assuming, however, that the substance of both is of the same density. . . . The sphere of the Attractive virtue which is in the moon extends as far as the earth, and entices up the waters; but as the moon flies rapidly across the zenith, and the waters cannot follow so quickly, a flow of the ocean is occasioned in the torrid zone towards the westward."

The invention of the telescope independently by Galileo (1564-1642) in 1609 enabled ocular demonstration of the correctness of the Copernican theory to be obtained. Almost the first observations made with the new instrument led to the discovery of the satellites of Jupiter by Galileo, and the determination of their periods of revolution round their primary, by Kepler, while shortly afterwards Galileo asserted that "*Cynthiae figuras æmulatur mater amorum*," i.e. Venus imitates the phases of the moon, as had been deduced by Copernicus. The invention of the telescope and almost simultaneously that of logarithms by Napier (1550-1617) in 1614 now enabled practical astronomy to make rapid strides. In 1629 Kepler in his *Notice to the Curious in Things Celestial*, warned astronomers of approaching transits, and in 1631 Gassendi (1592-1655) in Paris, observed the passage of Venus across the sun's disc and thus definitely established the fact that Venus described an orbit between the earth and the sun.

So far, however, astronomy had only been concerned with the gathering of facts, and Bacon's dream of a living astronomy by which the physical laws governing terrestrial

phenomena should be extended to the phenomena of the whole cosmic universe was by no means realised. To do this it was necessary that the relations between forces and motion should be discovered. Mechanics, so far, had merely been the study of equilibrium ; by introducing the notions of force, momentum and acceleration, Galileo performed the first great step in the development of dynamical science which was, in time, to lead to the evolution of physical astronomy. The general ideas necessary for such development were, so to speak, in the air. Gravitation was vaguely surmised by many as the force maintaining planets in their orbits, though it was very often confused, as in the case of Kepler, with ideas of magnetic vortices and emanations probably having their origin in the works of Gilbert (1544-1603) and Descartes (1596-1650). Galileo seems at times to have approached very near to the ideas of Newton on this subject, as the following passage shows, though his works indicate that he was not very clear or consistent in his opinions. "The parts of the earth have such a leaning towards its centre (i.e. the sun) that when it shifts its position these aforesaid parts, although far from the globe at the time of its shift, will follow it everywhere ; an example of this is the continual following of the Medicean stars (i.e. Jupiter's satellites) although continually separated from Jupiter. The same, indeed, must be said of the Moon obliged to follow the Earth."

It was reserved for Newton to give logical and mathematical form to these vague notions and to show that Kepler's three laws and the facts of observational astronomy could be deduced from the dynamical principles which he himself established. These led to the publication in 1687 of the *Philosophiæ Naturalis Principia Mathematica*, and their application to the description of the "system of the world." It is with the development of Mechanics to this point that it is now proposed to proceed.

The origin of Mechanics is to be found in the attempts made to explain the mode of action of the various instruments or machines invented by man for the purpose of performing work, and to explain the phenomena of motion. The use of the lever, inclined plane and the wedge, seems to date from the very dawn of history.

In the *Mechanica* of Aristotle (384-322 B.C.) references are made to the lever and the possibility of great weights being moved by small ones. The principle or law of the lever, that the weight moved and the moving force are in inverse proportion to their distances from the point of support or fulcrum of the lever seems to have been well known from the earliest times, but the reason for it is attributed to the weight (or force) which acts at the greater distance from the fulcrum "describing a greater circle" than the other, and that in consequence it moves the other weight more easily.

Archimedes (287-212 B.C.) appears to be the first who attempted any explanation of the lever based on mathematical principles. His work was composed in the same manner which Euclid used with such success in geometry. As postulates in his treatise *On Plane Equilibriums* he assumes that equal weights at equal distances are in equilibrium, and at unequal distances are not in equilibrium, that if when weights are in equilibrium something is added or subtracted from one of the weights, the system will incline towards the weight which is added to or from which nothing is taken away. In addition he assumes certain properties of the centre of gravity. This would seem to complicate matters, but to the mind of Archimedes and his contemporaries it is probable that the result of their geometrical training was to make the postulates seem more plausible than the result which he was demonstrating. From these postulates he then deduces the conditions of equilibrium for unequal weights, proving them first for commensurable and then for incommensurable magnitudes.

He also established the principles of hydrostatics in his work *On Floating Bodies*, basing his investigations on the following two postulates:—

1. "Let us assume that a fluid has the property that, if its parts lie evenly and are continuous, the part which is less compressed is expelled by that which is more compressed, and each of its parts is compressed by the fluid above it perpendicularly unless the fluid is shut up in something and compressed by something else."

2. "Let us assume that any body which is borne upwards in water is carried along the perpendicular (to the

surface) which passes through the centre of gravity of the body."

He then deals with the effects of placing solids in fluids, and shows that solids lighter than the fluid in which they are placed, are not completely immersed, but only so far as to displace a quantity of fluid equal to their own weight, and that if forcibly immersed a solid would be subject to an upward force equal to the difference between its own weight and that of the displaced fluid. Hence he deduced that solids heavier than the fluid, if weighed in the fluid, would appear lighter than their true weights by the weight of the fluid displaced. Without actually using a special term he considers the specific gravities of bodies, as he calls a body lighter than a fluid if its weight is less than that of an equal volume of the fluid.

Very little advance occurred in Mechanics for the next 1700 years until Leonardo da Vinci (1452-1519) and Stevinus of Bruges (1548-1620) again dealt with the lever and the equilibrium of three forces in a plane. Da Vinci also had clearer notions than his contemporaries as to the nature of forces, and anticipated Galileo in certain of his experiments on the falling of bodies down inclined planes.

The principle of the impossibility of perpetual motion played a great part in the investigations of these early philosophers, and indeed from this principle they derived most of their results. Stevinus, in his work, *Hypomnemata mathematica—De statica*, treats of the equilibrium of bodies on inclined planes. He discusses the equilibrium of an endless cord to which at equal distances apart fourteen balls of equal weight are attached, and considers what happens when they are hung over a triangular prism one side of which is horizontal. In the figure illustrating his argument he shows four balls on one side of the prism and two on the other, the remaining ones hanging symmetrically with respect to the base of the prism. Stevinus then concludes that the balls hanging symmetrically do not affect the equilibrium and that the four balls on one plane equilibrate the two on the other. For if the equilibrium be for a moment disturbed, it could never subsist, or as he writes: "But if this took place, our row or ring of balls would come once more into their original position, and from the same cause the eight globes to the left would

again be heavier than the six to the right, and therefore these eight would sink a second time and these six rise, and all the globes would keep up, of themselves, a continuous and unending motion, which is false." From this he then easily deduces the laws of equilibrium on the inclined plane and the triangle of forces.

In the chapter *De Hydrostatia* of the same work he deduces the principles of hydrostatics from the principle that "a given mass of water preserves within water its given place. . . . For, assuming it to be possible by natural means, let us suppose that A does not preserve the place assigned to it, but sinks down to D. This being posited, the water which succeeds A will for the same reason also flow down to D; A will be forced out of its place in D; and thus this body of water, for the conditions in it are everywhere the same, will set up a perpetual motion which is absurd."

It is to Stevinus also that we are indebted for the idea so fruitful in modern mechanics that the equilibrium of a system is not changed by the addition of rigid connections, and also for the enunciation of the principle of virtual motions or virtual velocities. In the *Trochleostatica* of the above-mentioned work, he writes: "Observe that this axiom of statics holds good here: As the space of the body acting is to the space of the body acted upon, so is the power of the body acted upon to the power of the body acting."

Thus the laws of statics or the science of equilibrium were placed on a sound basis by the work of Stevinus and da Vinci, and we must now consider the development of correct ideas with regard to dynamics or the science of motion.

The Aristotelian doctrines of motion had been accepted for nearly twenty centuries, and it was reserved for Galileo Galilei (1564-1642) to question these ideas, to show their insufficiency, and to establish certain of the laws of motion on which the further development of nearly all physical science has rested. According to the Aristotelian theory bodies fell to the earth because each body sought its natural place under the influence of its intrinsic property of heaviness, so that heavy bodies were supposed to fall faster than light bodies in the proportion of their relative weights. To an incredulous group of supporters of the Aristotelian ideas,

Galileo simultaneously dropped weights of different substances from the top of the leaning tower of Pisa, and showed that they all arrived at the bottom at practically the same instant, the small differences being correctly attributed to the different resistances of the air to the motion of bodies of different shape. Having visibly demonstrated that the old notions were false, he then experimented to find the law according to which bodies did fall. Thus instead of enquiring, as did the Aristotelians, *why* bodies fall, he set himself the problem of finding out *how* bodies fall, leaving the former question to be settled later. It is this attitude of Galileo towards phenomena, that of enquiring *how* before *why*, which has characterised all physical research subsequent to his time and has led to his being regarded as the founder of experimental physics. His investigations on the motions of bodies are set forth very clearly in his *Discorse e Dimostrazione Matematiche, intorno a Due Nuove Scienze* in 1638, though many of the results given there were obtained by him from experiments carried out between 1602 and 1604. In the introduction to the third Dialogue "On Local Motion" he writes as follows: "We promote a very new Science, but of a very old Subject. There is nothing in Nature more antient than *Motion*, of which many and great Volumns have been written by Philosophers: But yet there are sundry symptoms and Properties in it worthy of our Notice, which I find not to have been hitherto observed, much lesse demonstrated by any. Some slight particulars have been noted: as that the Natural Motion of Grave Bodies continually accellerateth, as they descend towards their Center: but it hath not been as yet declared in what proportion that Acceleration is made. For no man, that I know, hath ever demonstrated, That there is the same proportion between the spaces, thorow which a thing moveth in equal Times, as there is between the Odde Numbers which follow in order after a Unite. It hath been observed that Projects (or things thrown or darted with violence) make a Line that is somewhat curved; but that this Line is a Parabola, none have hinted: Yet these, and sundry other things, no lesse worthy of our knowledge, will I here demonstrate: And which is more, I will open a way to a most ample and excellent Science, of which these

Labours shall be the Elements: into which more subtil and piercing arts than mine, will be better able to dive."

Bodies falling freely in space moved too quickly for measurements to be made on their velocities, so Galileo simplified the process by investigating the motion of bodies down inclined planes. The accurate measurement of time was rather difficult in his day, so as a preliminary he devised a water clock in which equal times were defined as those in which equal quantities of water issued from an orifice under the action of a head of water. He first supposed that as the velocity of descent down the planes very clearly increased as a body descended it, the law regulating the rate at which its velocity increased was the most simple one, that is the velocity received equal additions for equal additions of distance along the plane traversed by it, or that the velocity was proportional to the distance travelled; but this supposition he showed did not agree with his experiments. Then on the next simplest hypothesis, that the velocity increased uniformly with the time, he showed that the distance travelled by a body in falling down the plane should be proportional to the square of the time, that is, if it fell 1 foot in one second it should fall 4 feet in two, 9 feet in three, and so on. His experiments on the plane agreed with this hypothesis, and he further proved that accepting this result no other hypothesis was in agreement with it.

He also showed that a body falling down an inclined plane would run up another inclined plane of any angle to approximately the same height as that at which it started on the first plane, from which he deduced that the height alone mattered, and that a body falling freely would acquire the same velocity as any other body falling on an inclined plane of any angle provided the total heights descended were the same in the two cases. This deduction then led him to his most important contribution to physical science—the law of inertia. In his own words from the *Discourses*, we read, "I take it for granted that the velocities acquired by a body in descent down planes of different inclination are equal if the heights of those planes are equal . . . but I wish to go further and by an actual experiment so as to increase the probability of it that it shall amount almost to an absolute demonstration. Suppose this sheet of paper

to be a vertical wall, and from a nail driven in it a ball of lead weighing two or three ounces to hang by a very fine thread AB 4 or 5 feet long. On the wall mark a horizontal line DC perpendicular to the vertical AB, which latter ought to hang about two inches from the wall. If now the thread AB with the ball attached take the position AC (inclined at an angle to AB) and the ball be let go, you will see the ball first descend through the arc CB and passing beyond B rise through the arc BD almost to the level of the line CD, being prevented from reaching it exactly by the resistance of the air and of the thread. From this we may truly conclude that its impetus at the point B, acquired by its descent through the arc CB, is sufficient to urge it through a similar arc BD to the same height. Having performed this experiment and repeated it several times, let us drive in the wall, in the vertical AB, as at E or at F, a nail five or six inches long, so that the thread AC, carrying as before the ball through the arc CB, at the moment it reaches the position AB, shall strike the nail E, and the ball be thus compelled to move up the arc BG described about E as centre. Then we shall see what the same impetus will here accomplish, acquired now as before at the same point B, which then drove the same moving body through the arc BD to the height of the horizontal CD. Now gentlemen, you will be pleased to see the ball rise to the horizontal at the point G, and the same thing also happen if the nail be placed lower as at F, in which case the ball would describe the arc BJ, always terminating its ascent precisely at the line CD. . . . This experiment leaves no room for doubt as to the truth of the supposition. For as the two arcs CB, DB are equal and similarly situated, the momentum acquired in the descent of the arc CB is the same as that acquired in the descent of the arc DB ; . . . so that in general every momentum acquired in the descent of an arc is equal to that which causes the same moving body to ascend through the same arc ; but all the momenta which cause the ascent of all the arcs BD, BG, BJ, are equal since they are made by the same momentum acquired in the descent CB, as the experiment shows, therefore all the momenta acquired in the descent of the arcs DB, GB, JB, are equal."

Later on we read : " It is plain now that a moveable body,

starting from rest at A and descending down the inclined plane AB, acquires a velocity proportional to the increment of its time ; the velocity possessed at B is the greatest of the velocities acquired, and by its nature immutably impressed, provided all causes of new acceleration or retardation are taken away : I say acceleration, having in view its possible further progress along the plane extended ; retardation, in view of the possibility of its being reversed and made to mount the ascending plane BC. But in the horizontal plane GH its equable motion, according to its velocity as acquired in the descent from A to B, will be continued *ad infinitum*."

As a result of Galileo's great discovery that a body left to itself continues in motion in a straight line with constant velocity, the whole problem of motion acquired a new aspect. Whereas formerly, according to the peripatetics, motion in a circle was the most natural motion as it was the most perfect and, consequently, it was idle to pursue enquiries regarding its origin ; what now required explanation was the deviation from motion in a straight line. As a result, the notion gradually arose of a force drawing the planets towards the sun, and we have seen earlier in the chapter how Galileo expressed himself on this matter.

Another important contribution to science made by Galileo was the principle of the parallelogram of velocities, which he applied with great astuteness to the motion of projectiles. It had previously been thought that a body could have one only motion at a time, so that it was considered that a projectile moved in a straight line until the force propelling it was expended, and that it then fell suddenly to the ground. This difficulty regarding the co-existence of two motions had led many to deny the truth of the Copernican theory in which the earth was held to have translatory and rotational movements at the same time. In the case of projectiles, Galileo showed that the path described could be deduced from the knowledge of the initial velocity, which would remain constant, by superposing on such motion that of a body falling freely under gravity in accordance with the laws discovered by himself. This led to the discovery of the parabolic path, which Galileo illustrated by reference to the paths of bodies dropped from the masts of ships, which he showed were

straight lines relative to the moving ship, but parabolas with reference to axes at rest.

Galileo was also responsible for the study of pendulum motion which played a large part in the history of mechanics during the fifty years after his death. The isochronism had been observed by others, but he rediscovered it himself very early in his career, and tested it by counting his pulse beats, and at once saw that it could be used as a measure of time and even seems to have considered the possibility of its application in clocks. Further experiment established the fact that the period of vibration was proportional to the square root of the length of the pendulum. Mersenne (1588-1648) in 1644 determined the length of a simple pendulum beating seconds and proposed the difficult problem of determining the length of a simple pendulum isochronous with a given compound pendulum. The invention of the pendulum clock in 1657 by Huygens provided a reliable means of measuring time, and immediately had an effect in largely increasing the accuracy of astronomical observations and so enabled the new science of dynamics to attain an exactness the lack of which, no doubt, was largely responsible for the lateness of its development.

It is to Huygens (1629-1695) that the next important additions to our knowledge of mechanics are due. In many respects it may be said that the mantle of Galileo fell upon his shoulders. He seems to have formed a clearer conception of the law of inertia than did Galileo. In his *Horlogium oscillatorium*, published in 1673, he states as a hypothesis, "If gravity did not exist, nor the atmosphere obstruct the motions of bodies, a body would keep up for ever the motion once impressed upon it, with equable velocity, in a straight line." He also determined the length of the seconds pendulum and deduced the value of $g/2$, the distance of free fall of a body from rest in one second, which was then used instead of g in mathematical calculations. His value was 15 Paris feet 1 inch 1 line $7/9$ which gives g in English feet as 32.16 .

Huygens, about this time, investigated the theory of uniform motion in a circle, and also solved Mersenne's problem of the compound pendulum. To do the latter, which was a very difficult problem, and was, in fact, the first

solution of a problem involving the consideration of the motion of a rigid body, he generalised the principle of Galileo respecting the heights of ascent. In his *Horlogium oscillatorium* (1673) we read, "If any number of weights be set in motion by the force of gravity, the common centre of gravity of the weights as a whole cannot possibly rise higher than the place it occupied when the motion began. That this hypothesis of ours may arouse no scruples, we will state that it simply imports, what no one has ever denied, that heavy bodies do not move *upwards*—and truly if the devisers of the new machines who make such futile attempts to construct a perpetual motion would acquaint themselves with this principle, they could easily be brought to see their errors and to understand that the thing is utterly impossible by mechanical means." And later on, "If a pendulum, composed of several weights, set in motion from rest, complete any part of its full oscillation, and from that point onwards the individual weights, with their common connections dissolved, change their acquired velocities and ascend upwards as far as they can, the common centre of gravity of all will be carried up to the same altitude with that which it occupied before the beginning of the oscillation."

On this generalisation of Galileo's principle respecting a single mass applied to a system of masses, Huygens founded his theory of the compound pendulum and the theory of the centre of oscillation.

Huygens was also one of the three "greatest Geometers" who solved the problem of impact which had been proposed by the Royal Society. Wallis (1616-1703) considered the impact of inelastic bodies while Wren (1632-1723) and Huygens each dealt with elastic bodies only. Wren also carried out experiments to test his results which were practically the same as those of Huygens. All three established the principle of the conservation of linear momentum and showed the importance of the product of the mass and velocity jointly, while it is probably due to this work that the concepts of mass and momentum, required for later developments, were rendered clear and definite.

It is to Sir Isaac Newton (1642-1727) more than any other that we owe the consolidation of all the views which

were current previous to his time. In doing this he had to invent new methods of mathematical analysis as the mathematics of his time was quite incapable of dealing with the complicated problems which he solved. His invention of the method of fluxions, or as it is now called, the infinitesimal calculus, provided the mechanism for the investigation of continually varying quantities, without which further progress would have been almost impossible. The results of his work are incorporated in his *Mathematical Principles of Natural Philosophy*, a work which as an exhibition of individual intellectual effort is unsurpassed in the history of the human race.

Newton's thoughts were very early directed to the study of motion, and in particular to the motion of the planets and the operation of Kepler's Laws. In 1665, when a young graduate of Cambridge, driven into retirement in Lincolnshire by the Great Plague, he seems to have commenced the investigations which culminated twenty-two years later in the publication of the *Principia*. Others besides Newton were interested in the nature and causes of planetary motion, and we have seen how vague ideas respecting the existence of forces between planets and their primaries, and between falling objects and the earth had been suggested, but so far there had been no definiteness or quantitative character associated with these ideas apart from the observed fact that all bodies fell to the ground with the same acceleration. In this connection we have Newton's own statement written in 1714 respecting the origin of his work, which as a summary of the accomplishments of two years is probably unequalled. "In the beginning of the year 1665 I found the method of approximating Series and the Rule for deducing any dignity of any Binomial into such a Series. The same year in May I found the method of tangents of Gregory and Slusius, and in November had the direct method of fluxions, and in the next year in January had the Theory of Colours, and in May following I had entrance into y^e inverse method of fluxions. And the same year I began to think of gravity extending to y^e orb of the Moon, and having found out how to estimate the force with w^{ch} (a) globe revolving within a sphere presses the surface of the sphere, from Kepler's Rule of the periodical times of the Planets being in a sesquialterate

proportion of their distances from the centre of their Orbs, I deduced that the forces w^{ch} keep the Planets in their Orbs must (be) reciprocally as the squares of their distances from the centres about which they revolve: and thereby compared the force requisite to keep the Moon in her Orb with the force of gravity at the surface of the earth, and found them answer pretty well. All this was in the two plague years of 1665 and 1666, for in those days I was in the prime of my age for invention, and minded Mathematicks and Philosophy more than at any time since."

By the force with which a globe revolving in a sphere presses the surface of the sphere Newton means the "centripetal force" as it was called, involved in uniform circular motion, which had been first discovered by Huygens, though Newton later on in the same statement mentions that "he had it" independently. The "pretty nearly" in the above quotation, while not destroying Newton's faith in the theory was, however, sufficient to prevent his publication of his results. Observation of the moon showed that it was deflected from the tangent of the orbit at any point by about 13 feet in one minute, whereas his calculations gave about 15 feet. As a result "he laid aside at that time any further thought of the matter." Later, about 1669, owing to correspondence with Hooke regarding the paths of falling bodies taking the axial motion of the earth into account, he again became interested in the matter and approached it with greater confidence as he was able to show that on the assumption of the inverse square law the force exerted by a sphere at external points was exactly the same as if its whole mass were concentrated at the centre, and thus rendered strictly accurate the calculations which previously he had considered only approximate. In addition, the French scientist Picard (1620-1682), had made a redetermination of the length of a degree of latitude, and found it to be 69.1 miles as compared with the 60 miles used in Newton's former calculation. The discrepancy between the two results now disappeared and he regarded his ideas as fully confirmed. His own description of the argument is given below, taken from Book III of the *Principia*.

"The mean distance of the moon is . . . about $60\frac{1}{2}$ semi-diameters of the earth. . . . Let us assume the mean dis-

tance of 60 diameters in the syzygies ; and suppose one revolution of the moon in respect of the fixed stars, to be completed in $27^d\ 7^h\ 43'$, as astronomers have determined, and the circumference of the earth to amount to 123,249,600 Paris feet as the French have found by mensuration. And now if we imagine the moon, deprived of all motion, to be let go, so as to descend towards the earth with the impulse of all that force by which it is retained in its orb, it will, in the space of one minute of time, describe in its fall $15^{1/12}$ Paris feet. . . . For the versed sine of that arc, which the moon, in the space of one minute of time, would by its mean motion describe at the distance of 60 semi-diameters of the earth is near $15^{1/12}$ Paris feet, or more accurately, 15 feet 1 inch and 1 line $\frac{4}{9}$. Wherefore, since that force, in approaching the earth, increases in the reciprocal duplicate proportion of the distance, and upon that account, at the surface of the earth, is 60×60 times greater than at the moon, a body in our regions, falling with that force ought, in the space of one minute of time, to describe $60 \times 60 \times 15^{1/12}$ Paris feet ; and, in the space of one second of time, to describe $15^{1/12}$ of those feet ; or more accurately 15 feet, 1 inch, and 1 line $\frac{4}{9}$. And with this very force we actually find that bodies here upon earth do really descend ; for a pendulum oscillating seconds in the latitude of Paris will be 3 Paris feet, and 8 lines $\frac{1}{2}$ in length, as Mr. Huygens has observed. And the space which a heavy body describes in falling in one second of time is to half the length of this pendulum in the duplicate ratio of the circumference of a circle to its diameter (as Mr. Huygens has also shown), and is therefore 15 Paris feet, 1 inch, 1 line $\frac{7}{9}$. And therefore the force by which the moon is retained in its orbit becomes at the surface of the earth, equal to the force of gravity which we observe in heavy bodies there."

Thus, shortly after 1669 Newton seems to have been in the possession of the main ideas of his theory of gravitation, and it is likely that by this time he had been able to prove the following propositions with regard to motion under the influence of a centripetal force :—

1. That Kepler's Second Law regarding the conservation of areas held for motion under the influence of a centripetal force.

2. That if an ellipse were described the law of force was the inverse square ; and

3. That the orbit of a particle projected under a central force varying as the inverse square of the distance was an ellipse with the centre of force as a focus, i.e. Kepler's First Law.

He does not appear to have published his results, for in 1684 Halley (1656-1742), who "from considerations of the sesquialter proportion of Kepler, concluded that the centripetal force decreased in the proportion of the squares of the distances reciprocally," but was unable to deduce the motion from the law, enquired of Newton what the orbit would be under such a force. Newton to the surprise of Halley was immediately able to announce that the orbit would be an ellipse. Halley, from this time onwards, became very interested in the publication of Newton's work, so that eventually, largely as a result of his own diligence and finally through the defrayment of the cost of publication, he was able to announce to the Royal Society "that his worthy contryman Mr. Isaac Newton has an incomparable treatise of motion almost ready for the press" and that the law of the inverse square "is the principle on which Mr. Newton has made out all the phenomena of the celestial motions so easily and naturally, that its truth is past dispute." Finally, in 1687, the *Principia* appeared.

In this treatise Newton consolidated the views prevalent in his time, into one logical and coherent system, starting with definitions and laws based on the facts of experience and extending them propositionally to include most of the phenomena of the universe. The nature and scope of the work is excellently described in the following passage from a contemporary reviewer, probably Dr. Halley, in the *Philosophical Transactions* of the Royal Society for the year 1687 :—

"This treatise is divided into three books, whereof the first two are entitled *de Motu Corporum*, the third *de Systemate Mundi*. The first begins with definitions of the terms made use of, and distinguishes time, space, place, and motion, into absolute and relative, real and apparent, mathematical and vulgar ; showing the necessity of such distinctions. To these definitions are subjoined the laws of motion, with several corollaries from them ; as concerning

the composition and resolution of any direct force out of, or into any oblique forces, by which the powers of all sorts of mechanical engines are demonstrated ; the laws of the reflection of bodies in motion after their collision ; and the like.

“ These necessary præcognita being delivered, our author proceeds to consider curves generated by the composition of a direct impressed motion with a gravitation or tendency towards a centre ; and having demonstrated that in all cases the areas at the centre, described by a revolving body, are proportional to the times ; he shows how, from the curve described, to find the law or rule of the decrease or increase of the tendency or centripetal forces as he calls it, in different distances from the centre. Of this there are several examples ; as, if the curve described be a circle passing through the centre of tendency ; then the force or tendency towards that centre is in all points as the 5th power, or squared-cube, of the distance from it reciprocally ; if in the proportional spiral, reciprocally as the cube of the distance : if in an ellipse about the centre of it directly as the distance. If in any of the conic sections about the focus ; then he demonstrates that the vis centripeta, or tendency towards that focus, is in all places reciprocally as the square of the distance from it ; and that according to the velocity of the impressed motion, the curve described is an hyperbola ; if the body moved be swift to a certain degree, then a parabola ; if slower, an ellipse, or a circle in one case. From this sort of tendency or gravitation it follows likewise, that the squares of the times of the periodical revolutions, are as the cubes of the radii or transverse axes of the ellipses. All which being found to agree with the phenomena of the celestial motions, as discovered by the great sagacity and diligence of Kepler, our author extends himself upon the consequences of this sort of vis centripeta ; showing how to find the conic section which a body shall describe when projected with any velocity in a given line, supposing the quantity of the said force known ; and laying down several neat constructions to determine the orbs. . . .

“ Next the motion of bodies in given surfaces is considered, as likewise the oscillatory motion of pendules ; where it is shown how to make a pendulum vibrate always in equal

times, though the centre or point of tendency be never so near; to which the demonstration of Mr. Huygens de Cycloide is but a corollary. And in another proposition is shown the velocity in each point, and the time spent in each part of the arch described by the vibrating body. After this, the effects of two or more bodies, towards each of which there is a tendency, is considered; and it is made out that two bodies, so drawing or attracting each other, describe about the common centre of gravity, curve lines, like to those they seem to describe about each other.

“This done, our author, with his usual acuteness, proceeds to examine into the causes of this tendency or centripetal force, which from undoubted arguments is shown to be in all the great bodies of the universe. . . .

“The third and last book is entitled *de Systemate Mundi*, wherein the demonstrations of the two former books are applied to the explication of the principal phænomena of nature; here the verity of the hypothesis of Kepler is demonstrated; and a full resolution given to all the difficulties that occur in the astronomical science; they being nothing else but the necessary consequences of the sun, earth, moon, and planets, having all of them a gravitation or tendency towards their centre proportional to the quantity of matter in each of them and whose force abates in duplicate proportion of the distance reciprocally. Here likewise are indisputably solved the appearances of the tides, or flux and reflux of the sea; and the spheroidal figure of the earth and Jupiter determined from which, the precession of the equinoxes, or rotation of the earth's axis is made out, together with the retrocession of the moon's nodes, the quantity and inequalities of whose motion are here exactly stated a priore.

“And it may be justly said, that so many and valuable philosophical truths, as are herein discovered and put past dispute, were never yet owing to the capacity and industry of any one man whatever.”

The foundations of the Newtonian, or, as it is sometimes called, the Galileo-Newtonian system, are in the *Axiomata sive Leges Motus*. These are given below:—

Law I. Every body continues in its state of rest or of uniform motion in a straight line, except in so far as

it may be compelled by impressed forces to change that state.

Law II. Change of motion is proportional to the impressed force, and takes place in the direction of the straight line in which the force acts.

Law III. To every action there is always an equal and contrary reaction: or, the mutual actions of any two bodies are always equal and oppositely directed.

Scholium to Law III. If the action of an agent be measured by the product of its force into its velocity; and if, similarly, the reaction of the resistance be measured by the velocities of its several parts into their several forces, whether these arise from friction, cohesion, weight or acceleration, action and reaction, in all combinations of machines, will be equal and opposite.

In contradistinction to the axioms of Geometry these laws must be considered as resting on the results of observation and experiment, and not on our intuition.

The first law describes a test for the presence of external forces, the second shows how an external force may be measured, while the third law relates the two aspects of the action between two bodies.

The first law immediately brings us into contact with a difficulty, for the velocity mentioned in this law can only be the velocity referred to a system of axes in absolute rest. The postulation of an absolute space by Newton (though he admitted the difficulty of identifying it) at once aroused criticism from various philosophers, particularly Leibnitz (1646-1716), but without any suggestions of possible alternatives from any of them. We shall not, however, deal with this any further at this point, but shall leave it for the consideration of a later chapter, when it will be seen how the development of electrodynamics has made it of supreme importance.

In the second law Newton means by motion what is now called momentum, in which the quantity of matter involved in the motion is considered, and by impressed force what is now called impulse, in which the time during which the force acts, is taken into account. A further consideration

of the law leads to enquiry as to the definitions of equal masses, of equal quantities of matter and of equal forces. That the weight of a body was not a constant seems to have been known quite early in the history of pendulum motion, for the variation in length of the seconds pendulum at different places on the earth's surface was well known in 1660, while in 1662 efforts were made to determine a change of weight with change of level, though in this case no change was detected. In dynamics, matter is considered in no other way except as that which can have its motion changed by the application of force. Thus Newton conceived quantities of matter equal if they suffered the same changes of motion under the action of the same forces, and conversely forces were equal if they produced the same changes of motion in the same body. In this way, then, Newton was able to distinguish clearly between the weight of a body and its mass. Thus the masses of bodies are proportional to the forces which produce equal accelerations in them. Now under the action of their own weights all bodies fall to the ground at the same place with the same acceleration, so that the masses of bodies are proportional to their weights at the same place. Thus the fact that the weight of a body remains constant at the same place acquires a wider import, for it means that the mass of the body is constant, and this holds whatever physical changes it undergoes.

Newton proved this very accurately by means of pendulum experiments. He writes : " It has been, now of a long time, observed by others, that all sorts of heavy bodies (allowance being made for the inequality of retardation, which they suffer from a small power of resistance in the air) descend to the earth *from equal heights* in equal times ; and that equality of times we may distinguish to a great accuracy, by the help of pendulums. I tried the thing in gold, silver, lead, glass, sand, common salt, wood, water, and wheat. I provided two wooden boxes, round and equal. I filled the one with wood, and suspended an equal weight of gold (as exactly as I could) in the centre of oscillation of the other. The boxes hanging by equal threads of eleven feet, made a couple of pendulums perfectly equal in weight and figure, and equally receiving the resistance of the air. And placing the one by the other, I observed them

to play together forwards and backwards, for a long time, with equal vibrations. And therefore the quantity of matter in the gold (by Cor. 1 and 6, prop. 24, book 2) was to the quantity of matter in the wood, as the action of the motive force (or *vis motrix*) upon all the gold, to the action of the same upon all the wood; that is, as the weight of the one to the weight of the other. And the like happened in other bodies. By these experiments, in bodies of the same weight, I could manifestly have discovered a difference of matter less than a thousandth part of the whole, had any such been."

The Third Law can be regarded as an extension of the First Law to a system of bodies. For the mutual forces in a system of two bodies cannot alter the state of rest or uniform motion of its centre of inertia, hence the change of motion of the one body must be equal and opposite to that of the other. Newton proved this law experimentally by placing a magnet in one vessel and a piece of iron in another, and floated both vessels on water so that they touched each other, and observed that as neither was able to move the other, the attraction of the magnet on the iron must be equal to the attraction of the iron on the magnet. He also pointed out a consequence of the denial of this law, for if the attraction of the earth on a mountain were less than that of the mountain on the earth there would be a residual force acting on the system which would in consequence move with a constantly accelerated velocity through space.

In the scholium to the Third Law Newton interpreted the law in an extended manner. In modern form the statement given above is equivalent to "the activity of an agent (or the rate at which it does work) is equal to the counter activity of the resistance." This method of interpretation is not very far removed from a statement of the Law of the Conservation of Energy.

From the observed motions of the planets Newton deduced that they attract each other according to a definite law. As a result of his calculations on the moon he was able to identify this attraction with the force which causes bodies at the surface of the earth to fall to the ground, and he thus provided the first proof of the applicability of terrestrial laws to cosmical phenomena.

In Book III of the *Principia* Newton extends the principle to all the matter of the universe in the Law of Gravitation to the effect that "Every particle of matter in the universe attracts every other particle with a force in the direction of the straight line joining them and whose magnitude is proportional to the product of their masses and inversely as the square of their distance apart." Thus the attraction of a mass m on a mass m' (i.e. the weight of each due to the other) is given by $\gamma mm'/d^2$ where d is their distance apart and γ is the constant of gravitation depending on the units in which the attraction, masses and distance apart are measured.

In the *Principia* Newton only considered what could be demonstrated, so that conjectures and speculations were rigidly kept out. Thus the *Principia* gives no clue to Newton's ideas of the mechanism of gravitation. The success of his dynamical system and law of gravitation in which the expressions for the forces depended only on the distances between points, and not on the space between them led to the idea of action at a distance, particularly in the late years of the eighteenth century when the new phenomena of electrostatics were beginning to be subjected to mathematical treatment of a somewhat similar kind. In this connection it is very interesting to have Newton's own views on such an important question, particularly on account of their bearing on the historical development of the theories of electricity and magnetism. In a letter to Bentley regarding action at a distance, he writes :—

"You sometimes speak of gravity as essential and inherent to matter. Pray do not ascribe that notion to me, for the cause of gravity is what I do not pretend to know, and therefore would take more time to consider of it.

"It is inconceivable that inanimate brute matter should without the mediation of something else which is not material, operate on and affect other matter without mutual contact as it must do if gravitation in the sense of Epicurus be essential and inherent in it. . . . That gravity should be innate, inherent, and essential to matter, so that one body may act upon another at a distance through a *vacuum*, without the mediation of anything else, by and through which their action and force may be conveyed from one to

another, is to me so great an absurdity, that I believe no man who has in philosophical matters a competent faculty of thinking, can ever fall into it. Gravity must be caused by an agent acting constantly according to certain laws; but whether this agent be material or immaterial, I have left to the consideration of my readers."

He did, however, later attempt to account for gravitation by means of differences of pressure in an æther, but he did not publish any theory because he "was not able from experiment and observation to give a satisfactory account of this medium, and the manner of its operation in producing the chief phenomena of nature."

The followers of Newton seem, in the majority of cases, to have been content with a knowledge of the truth of the law of gravitation without attempting to explain it further. In fact, the whole of natural philosophy was based on the law of the inverse square so that a theory was regarded as complete if it could be expressed in formulæ derivable from a law of force involving only the positions of the interacting bodies. This was particularly evident in the development of the theories of electrical and magnetic action, until the time of Faraday, who shared with Newton a great repugnance to the idea of action at a distance. We shall see in a later chapter how modern science has come to the conclusion that while it is still unphilosophical to assume that "any body can act where it is not," our ideas of phenomena as taking place in a three-dimensional space have had to be modified very considerably. In consequence, the motions of bodies by which the gravitating property was inferred still may be straight lines in a space whose properties are altered by the mere presence of bodies.

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CHAPTER III

MATTER AND THE CONSERVATION OF MASS

AMONG the earliest Greek philosophers who wrote on the nature of matter was Leucippus (*circa* 500 B.C.), who, adapting in part some of the views of Democritus (465-375 B.C.), suggested a theory of matter which is not very dissimilar from that which we have at the present day. Only references to the writings of Democritus have come down to us, but the Roman poet Lucretius (98-55 B.C.), in his poem *De Rerum Natura*, gives an account of the ideas of these two philosophers. The first principle in the theory was that nothing could arise out of nothing ; that nothing could be reduced to nothing. It was assumed that all matter consisted of an infinite number of atoms, so small as to be invisible and incapable of sub-division. Each of these atoms was considered to be incompressible, and to fill entirely the space it occupied. Different bodies differed in the arrangement of the atoms, while the only things that could exist were atoms and the "void"—a space absolutely empty. The compounds of the atoms were liable to change as the arrangement of the atoms changed, but the individual atoms did not change. The atoms were always moving, and in nature their different combinations or aggregations were brought about by a purely mechanical system as distinguished from the theory of Empedocles (*circa* 490-430 B.C.), in which love and hate were regarded as ruling over things.

In opposition to this view of the ultimate constitution of matter, the theory that matter consisted of one primordial stuff which was the habitat of the four elementary principles of earth, water, air and fire, was developed by Aristotle (384-322 B.C.) and his followers. These four constituted the four elements, but they were not elements in the sense that we now attach to the term. Rather were

they characteristics or properties of matter. Thus earth implied the properties of dryness and coldness; water, coldness and wetness; air, wetness and heat; and fire, dryness and heat. Substances differed from each other in their possession of different proportions of these elementary principles.

It was easy for anyone believing in these principles, and the whole of the civilised world did believe in them for many centuries after Aristotle, to consider the transmutation of matter as an event to be expected. If all the different substances consisted of one *prima materia* united with certain properties, it might be possible to remove these properties and so obtain the *prima materia* itself, and this by the addition of suitable properties might be made into something else.

This led to the alchemical ideal—the changing of metals into gold and silver, and so we have for many centuries this one idea as the motive power of nearly all chemical experiment down to comparatively modern times. It is not necessary to go into detail about the work of the alchemists, as apart from the discovery of new substances and improvements in methods of analysis and procedure, they provided very little in the way of a chemical theory. The following quotations from various alchemical writers will give some indication of their point of view:—

“It is necessary to deprive matter of its qualities in order to draw out its soul. Copper is like a man, it has a soul and a body, the soul is the most subtle part, . . . that is to say, the tinctorial spirit. The body is the ponderable, material, terrestrial thing endowed with a shadow. After a series of suitable treatments, copper becomes without shadow and better than gold. The elements grow and are transmuted, because it is their qualities, not their substances, which are contrary.”

“The only thing which distinguishes one metal from another is its degree of maturity, which is, of course, greatest in the most precious metals; the difference between gold and lead is not one of substance but digestion; in the baser metal the action has not been able to purge out its metallic impurities. If by any means this superfluous impure matter could be organically removed from the baser metals, they would become gold and silver. So

miners tell us that lead has in many cases developed into silver in the bowels of the earth, and we contend that the same effect is produced in a much shorter time by the means of our Art."

One modification of the Aristotelian doctrine brought about by the alchemists does, however, merit attention. This was the idea that while the elements earth, water, air and fire, were the ultimate elements, there were other proximate elements or principles which gave matter certain distinguishing characteristics. These were the principles of "mercury" and "sulphur," and to which was added later the principle of "salt." This "mercury" was not ordinary mercury, but "the mercury of the philosophers,"—the soul of mercury, which was the characteristic of metallic bodies, while the principle of "sulphur" was identified with the soul of combustibility and impurity, and "salt" with the principle of resistance to fire, or the principle of fixity. Gold, for example, was supposed to consist of very pure "mercury" united with a red "sulphur."

The recognition of these three principles represents a considerable advance on the four elements of Aristotle, as they were based on considerations of the behaviour of bodies in actual experience, rather than on the idea that nature must be simple and that therefore complex bodies must be built up of simple elements. Thus the alchemists were beginning to study the changes which matter undergoes, as well as the new substances derived from such changes.

In consequence there soon arose criticism of the Aristotelian doctrines which had lasted so long. Van Helmont (1577-1644) was the first definitely to deny the truth of the theories of the four elements and of the "*tria prima*." If any, air and water were regarded by him as being the primitive elements of things. Earth and fire were expressly stated not to be elements. That water could change into other substances he considered proved by his experiment of planting a willow weighing 5 lb. in 200 lb. of dry soil. In five years the willow increased in weight to 169 lb., while the weight of the soil was practically the same. He attributed the increase in weight to the water which had been absorbed and changed into wood, bark, and leaves. This experiment implied his belief that matter could neither be destroyed nor created. Though he still believed in the

transmutation of the elements, he is well entitled to be considered the first of the new chemists.

The work of the chemists succeeding Van Helmont was principally concerned with the elucidation of the phenomena of burning, and we shall now consider the work of three chemists who, as a result of their experiments, threw considerable light on the problem, though for various reasons their work did not meet with the notice and the assent of the rest of the scientific world of their day. In discussing their work it should be remembered that, in common with the rest of the world, they were hampered by their views on the nature of heat and fire which, whatever else they were considered, were certainly in most cases regarded as being material.

Jean Rey (seventeenth century), a French physician, about the year 1630 noticed that the effect of fire in the calcination of a metal was not a simplifying action as had previously been assumed. An increase in weight took place, and Rey assigned the increase in weight to the attachment of the particles of the air by the metal.

This work was followed about forty years after by that of Robert Boyle (1627-1691), who directed special attention to the part played by air in combustion. He was aware that charcoal, made in closed iron retorts, burned and became white ashes if the retorts were opened to the air before they had cooled sufficiently. He spoke of the air as a "menstruum," and said that in such operations as calcining "we may well take the freedom to examine . . . whether there intervene not a coalition of the parts of the body wrought upon with those of the menstruum, whereby the produced concrete may be judged to result from the union of both." He considered the air to be "a confined aggregate of effluvia from such differing bodies as exhalations from the earth, plants and animals, and subtle emanations from the earth's magnetism, that though they agree in constituting by their minuteness and motions one great fluid mass of matter, yet perhaps there is scarce a more heterogenous body in the world."

He also tried burning substances *in vacuo*, and found that a few would still burn. Gunpowder, for example, did, and he thought this might be due to air imprisoned in the nitre during crystallisation, so he recrystallised it *in vacuo* and

still found that it would burn. He was aware of the increase in weight which accompanied calcination, but his views as to the material nature of fire prevented him from reaching a definite conclusion. He assumed that in some cases the increase in weight was due to the "matter of fire" attaching itself to the substance heated, and so devised experiments for "arresting and weighing the fire particles."

John Mayow (1643-1679) repeated and continued the work of Boyle. In his tract *De sal-nitro et spiritu nitro-æreo* (1674), he described experiments made on burning substances *in vacuo*. Sulphur and camphor, he found would not burn unless they were mixed with nitre, so he concluded that the air and nitre have something in common which he called "spiritus nitro-æreus." He also attributed the increase in weight which occurred, to combination with this "spiritus," and showed that the "spiritus" was merely a portion of the air by means of the following experiment:—

Inside a large globular vessel inverted over water he placed a candle and also a bridge on which were suspended pans containing sulphur, camphor, etc. Before the candle was lit he was able to burn the contents of the pans by means of a lens; when, however, the candle had burned out he could no longer do this. The water, he noted, rose and filled approximately one-fifth of the vessel above the level of the outside water. Hence he concluded that the greater part of the air differed from nitre air, and could not support combustion.

Mayow never isolated oxygen, but he got very near to the truth about combustion, and it is very surprising that his immediate followers did not hit on the real solution of the problem. The work of these three, however, seems to have been unknown to the chemists of the next hundred years.

In connection with these attempts to explain combustion, the remarks of Hooke in his *Micrographia* (1665), deserve attention, although he does not give his reasoning nor any account of his experiments, merely promising to deal further with the matter if he has time: "The dissolution of sulphurous bodies is made by a substance, inherent and mixed with the air, which is like if not the same as the air fixed in nitre. It seems reasonable to think that there is no such thing as an element of fire, but that the shining

transcendent body we call fire is nothing else but a mixture of the air and volatile parts of the sulphurous body acting on each other while they ascend." Again, "The air is the universal dissolvent of all sulphurous bodies, the action of the dissolution of the body by the air produces that which we call fire. This action is performed with so great a violence and does so rapidly agitate the smallest parts of the combustible matter that it produces in the diaphanous medium of the air the pulse of light." Hooke thus had a notion of burning which is singularly in agreement with modern theory. He does not, however, appear to have reverted to this subject as he promised.

Besides his contributions to our knowledge of combustion, Boyle has further claims to consideration owing to his very free criticisms of the Aristotelian doctrines current among his contemporaries. These are contained in his book, *The Sceptical Chymist; or, Chymico-Physical Doubts and Paradoxes touching the Experiments whereby Vulgar Spagyrist are wont to Evince their Salt, Sulphur, and Mercury, to be the true Principles of Things*. This work was published in 1661, in the form of a dialogue chiefly between Themistius who argued in favour of the "*Vulgar Spagyrist*" and Carneades, who expressed the doubts and opinions of Boyle himself. In a summary of his position towards the end of the book, Carneades asserts:—

"Since, in the first place, it may justly be doubted whether or no the fire be, as chymists suppose it, the genuine and universal resolver of mixt bodies;

"Since we may doubt, in the next place, whether or no all the distinct substances that may be obtained from a mixt body by the fire were pre-existent there in the formes in which they were separated from it;

"Since also, though we should grant the substances separable from mixt bodies by the fire to have been their component ingredients, yet the number of such substances does not appear the same in all mixt bodies; some of them being resolvable into more differing substances than three, and others not being resolvable into so many as three;

"And since, lastly, these very substances that are thus separated are not for the most part pure and elementary bodies, but new kinds of mixts;

"Since, I say, these things are so, I hope you will allow

me to infer, that the vulgar experiments (I might perchance have added, the arguments too) wont to be alledged by chymists to prove, that their three hypostatical principles do adequately compose all mixt bodies, are not so demonstrative as to induce a wary person to acquiesce in their doctrine, which, till they explain and prove it better, will by its perplexing darkness be more apt to puzzle than satisfy considering men, and will to them appear incumbered with no small difficults."

Carneades argues with great spirit and illustrates all his arguments and doubts by reference to actual experiments, while Themistius relies on the authority of the peripatetics and pure reason; alleging that it is "much more high and philosophical to discover things *a priore* than *a posteriore*" as do the "sooty empirics."

Boyle was gradually approaching the scientific conception of chemical changes and always looking for "the true and fundamental causes of things." As a deduction from the discourse in *The Sceptical Chymist* he writes: "That it may as yet be doubted, whether or no there be any determinate number of elements; or, if you please, whether or no all compound bodies do consist of the same number of elementary ingredients or material principles." And later: "And to prevent mistakes I must advertise you, that I now mean by elements, as these chymists that speak plainest do by their principles, certain primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the ingredients of which all those called perfectly mixt bodies are immediately compounded, and into which they are ultimately resolved."

He thus unmistakably defines what he means by an element, though he was not able to suggest the tests which were to decide whether a body was an element or not. He also defines what he claims to be the aim of chemistry, i.e. the study of chemical composition when he writes: "It is now time to consider not of how many Elements it is possible that nature may compound mixt bodies, but (at least, as far as the ordinary experiments of chymists will inform us) of how she doth make them up."

Although such excellent work on combustion had been done, the enlightened views of these philosophers were not destined to be accepted. Another theory was to arise—

a mistaken one, which nevertheless held the attention of chemists for the next 120 years. Rey, Mayow and Boyle had explained in varying degrees of clearness and accuracy what happened in the calcining of metals, but the converse phenomenon of the reduction of calces by heating with charcoal and various other substances had not received any explanation at their hands. The new theory supplied this deficiency, and it is probably because of this fact that it thus appeared to embrace a wider field of phenomena, that it owed its rapid acceptance and the tenacity of its appeal even in the face of apparently contradictory facts. This was the phlogiston theory.

The origin of this theory is to be found in the writings of J. J. Becher (1635-1682), chiefly in his *Physica Subterranea* (1669). He was a believer in the "*tria prima*" which, however, he identified as the vitrifiable, the mercurial and the combustible earths. When a substance was burned he believed that the last of these, the "*terra pinguis*" was liberated. The idea was developed further by G. E. Stahl (1660-1734) into the theory of phlogiston, in a work published in 1717.

On this theory the fact that very many substances burned on being heated was attributed to their possession of a common property. They were all supposed to contain a fire element named phlogiston, which was expelled during burning, which was more or less violent in proportion to the amount of phlogiston in the substance. Combustible substances, therefore, were held to be compounds of phlogiston. Charcoal, sulphur, phosphorus and some other substances entirely disappeared on burning; hence they were held to be very rich in phlogiston. It was noticed that if certain of the products of combustion were heated in a closed space in the presence of these bodies, the original substance was very often re-obtained. Thus if a metal were burned, a calx was obtained and phlogiston was liberated (the metal being a compound of the calx and the phlogiston), whilst on heating the calx with charcoal the metal was again obtained. This fact was easily accounted for on the theory that charcoal was rich in phlogiston, and gave it up to the calx, so reforming the original metal.

The theory of phlogiston was very simple and it apparently explained what there was to explain. There were

difficulties ahead, however, but by suitable hypotheses these were surmounted. It was known, for instance, that the calx produced from the burning of a metal weighed more than the metal. The supporters of the phlogiston theory explained this by assuming that the fire element had negative weight, or even by using a fallacious application of Archimedes' principle, by stating that phlogiston was lighter than the air, so that when it was expelled from a metal, the metal lost buoyancy and so appeared heavier. The difficulty was not considered important as it was not realised at that time that the weight of a body was a definite property of a body, and that for the quantity of matter to be constant its weight should be constant. In any case the conspicuous fact was that heat left the burning bodies in far greater quantity than was supplied to start the burning.

Again, it was known that the production of calces could not take place in closed retorts. The phlogistonists, however, were equal to the occasion. They stated that the air had a limited capacity for absorbing phlogiston, and that on becoming saturated with phlogiston—being phlogisticated—combustion could no longer continue in it; and that phlogiston was expelled from substances in a rapid whirling motion which could not take place in a closed space.

Most of the chemists of the day accepted the theory, and under development it was extended to become a theory of chemical action. It was believed that in the corrosion of a metal by an acid, phlogiston was lost and the calx dissolved in the acid, the inflammable air produced being regarded by many as the "fire element" itself. The causticity of alkaline bodies was considered to be due to the presence of phlogiston in them. Mild alkali (or carbonated alkali) was supposed to be simpler than caustic alkali. When a solution of caustic lime was mixed with a solution of mild vegetable alkali (pot ashes) decomposition took place, mild lime being precipitated and caustic vegetable alkali left in solution. The mild alkali was considered to have taken up the principle of combustibility obtained by the caustic lime from the fire in its preparation from mild lime.

The first blow to the phlogiston theory was provided by Joseph Black (1728-1799). In his chemical researches on the fixed alkalis described in his paper, *Experiments upon*

Magnesia-alba, Quicklime and other Alkaline Substances, published in 1755, he showed that—

(i) when mild limestone was heated it lost weight and became caustic.

(ii) When the caustic lime was dissolved in water and treated with mild vegetable alkali the dried precipitate was limestone, and equalled in weight the mild limestone he started with.

(iii) When mild limestone was treated with acid an air was given off, whilst caustic limestone lost the property of evolving an air on treatment with acid. The gas which he collected he called "fixed air" as it appeared to be fixed in the mild limestone.

He performed similar experiments with *magnesia-alba*, and also investigated the production of caustic vegetable alkali from mild vegetable alkali, and concluded that the difference between caustic alkalis and mild alkalis depended on the "fixed air," and that it was not necessary to assume anything at all about phlogiston.

The importance of these experiments was immediately realised as it was seen that they constituted a formidable attack against the commonly accepted opinions. Throughout the investigation Black had systematically used the balance and so anticipated Lavoisier in his use of this instrument as the final arbiter in chemical investigation.

But other attacks on the phlogiston theory were shortly to arise. Black's work on the alkalis, and the discovery of a new kind of "air" gave a tremendous impetus to the study of gases, so that the period about to be described has been called the "pneumatic age of chemistry," and the investigators of gases "the pneumatic chemists."

Joseph Priestley (1733-1804), an amateur chemist, about 1767 began his investigations on "airs" which were to provide the material for the final overthrow of the phlogiston theory. Though Priestley discovered so many new substances and did so much to advance the study of chemistry in his day, he had a theory of working strangely at variance with what would be expressed by most other natural philosophers, inasmuch as he attributed all his discoveries to chance. Be that as it may "his random hazarding" and experiments were certainly accompanied by more discoveries and results than those of any other chemist of that period.

After having prepared many "airs" by the action of acids on metals, by allowing vegetables to decay, by heating various animal substances and showing great skill in the collection of them in his pneumatic trough, sometimes over water and sometimes over mercury, he at last prepared oxygen. He writes: "Having procured a lens of twelve inches diameter and twenty inches focal distance, I proceeded with great alacrity to examine by the help of it, what kind of air a great variety of substances, natural and factitious, would yield. . . . With this apparatus, after a variety of other experiments . . . on the 1st of August, 1774, I endeavoured to extract air from *mercurius calcinatus per se*; and I presently found that, by means of this lens, air was expelled from it very readily. Having got three or four times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express was, that a candle burned in this air with a remarkably vigorous flame . . . I was utterly at a loss to account for it." He found that mice could live longer in a closed space full of this air than in a similar closed space of ordinary air, and that it was evidently purer than ordinary air. Now Priestley was a confirmed phlogistonist, so he explained the phenomenon as best he could in terms of that theory. As combustion in ordinary air was supposed to take place until the air became saturated with phlogiston, this new "air," which allowed much more burning to take place in it than ordinary air must have less phlogiston in it to start with, nay, that possibly it had none at all. Arguing in this way he named the new air "dephlogisticated air."

At the same time as Priestley was making his experiments, Henry Cavendish (1731-1810) was also experimenting with "airs." Whilst Priestley had been experimenting in many directions, not so much with the object of testing theories as with the desire of making new discoveries, Cavendish was working slowly and methodically, accurately determining the composition of the air, and finding the specific gravities of the various "airs," even correcting for variations of temperature and barometric pressure. Priestley used to amuse his philosophical friends with experiments, chiefly, however, with the desire to impress them. His favourite experiment was to explode a mixture of "inflammable air

from metals " and " dephlogisticated air " in the proportion of two to one. A friend named Waltire drew attention to a dew which was formed on the sides of the containing vessel. This, Priestley says, confirmed a suspicion which he had, that the phlogistication of air would *deposit* moisture from the air. He repeated the experiment using a balance. The explosion took place in a stout glass vessel, and Priestley noticed a loss in weight. He then communicated with Cavendish, and says that the loss in weight must be the weight of the heat lost in the explosion and that this confirmed the notion that heat was a ponderable body. Priestley was at a loss to account for the dew containing an acid on some occasions.

In 1781 Cavendish, realising the importance of the phenomenon, repeated the experiments very carefully and showed that there was no loss in weight, and that the acidity was not always an accompaniment of the explosion. He published his results in the Philosophical Transactions for 1784, and writes : " From the fourth experiment it appears that 423 measures of inflammable air are nearly sufficient to phlogisticate 1000 measures of common air ; and that the bulk of the air remaining after the explosion is then little more than four-fifths of the common air employed ; so that, as common air cannot be reduced to much less bulk than that by any method of phlogistication, we may safely conclude that when they are mixed in this proportion, and exploded, almost all the inflammable air and about one-fifth part of the common air, lose their elasticity and are condensed into a dew which lines the glass.

" The better to examine the nature of the dew, 500,000 grain measures of inflammable air were burnt with about $2\frac{1}{2}$ times that quantity of common air and the burnt air made to pass through a glass cylinder eight feet long and three-quarters of an inch in diameter in order to deposit the dew. By this means upwards of 135 grains of water were condensed in the cylinder, which had no taste or smell, and which left no sensible sediment when evaporated to dryness ; neither did it yield any pungent smell during the evaporation ; in short it seemed pure water."

The experiment was made more conclusive by the use of dephlogisticated air in place of the common air, so that the proportion of inflammable air to dephlogisticated air was

as two is to one. Though not holding the phlogiston theory as strongly as some other philosophers, Cavendish was a phlogistonist, and he summed up his conclusions on these experiments by stating that dephlogisticated air is merely water deprived of its phlogiston, and that inflammable air is either pure phlogiston or phlogisticated water. At the same time he admitted that these experiments and "also most other phenomena of nature, seem explicable as well, or nearly as well" upon the Lavoisierian view.

We are now at the point in the history of chemistry at which Lavoisier placed it on the right path and which it has since followed. Before giving an account of the line of thought which led to Antoine Laurent Lavoisier (1743-1794) to give the correct theory of combustion, it will be convenient to treat of some of the earlier work of this great philosopher.

One of the most important of his early researches was on the alleged conversion of water into earth by heating, which was being discussed about that time (1770). Lavoisier heated a weighed quantity of eight times distilled rainwater in a closed weighed vessel for 101 days. At the end of that time a fine white sediment had collected at the bottom. The total weight of the vessel and water was, however, precisely the same as at the beginning, while on pouring off the water and sediment it was found that the vessel had diminished in weight by 17.4 grains. On evaporating the water Lavoisier found he had 20.4 grains of sediment, which he concluded came from the glass of the vessel. The difference between these weights he attributed to the solvent action of the water on the glass in which it was evaporated. By this investigation he destroyed the belief of the alchemists, and although he does not assert the principle of the indestructibility of matter, yet that is clearly to be inferred, both from the bold way in which he regarded his weighings as being conclusive that water was not changed to earth, and also by his being at great pains to construct a balance for this experiment far superior to any in use previously.

He later turned his attention to the problem of combustion, and repeated some of Rey's earlier work in which he found that no increase in weight takes place when metals are heated in closed vessels until they are opened and the

air rushes in. From these experiments he deduced that Boyle's idea of combustion being due to the fixation of the "igneous particles" could not be true, as there was no increase in weight while the vessel was closed. He also found that the increase in weight of the metal was equal to the weight of the air which rushed in. Hence he concluded that in the calcination of metals a portion of the air combined with the metal. The weighings he made indicated that about one-fifth of the weight of air in the closed vessel was fixed by the metal during the experiment. The results of these experiments were communicated to the French Academy in 1772.

In 1774 came Priestley's discovery of dephlogisticated air and his visit to Paris where he met Lavoisier. He mentions in his book, *Experiments and Observations on Different Kinds of Air*, published 1774-6-7, that he informed Lavoisier of his experiments with *mercurius calcinatus per se*. Lavoisier prepared this "air" and found that many of the products of combustion in it were acids, so he renamed it oxygen (acid producer). Shortly afterwards he carried out the experiments which enabled him in 1783 to advance a complete theory of combustion. In a memoir on the *Respiration of Animals* in 1777, he writes that he enclosed 50 cubic inches of common air in a vessel and introduced 4 ounces of very pure mercury which he proceeded to calcine during twelve days in a degree of heat almost equal to that which is necessary to make it boil. On the twelfth day, on allowing the vessel to cool, he observed that the air was diminished to the extent of from 8 to 9 cubic inches (about one-sixth of its bulk), and that 45 grains of *mercurius calcinatus per se* were formed. The air which was left did not precipitate lime water, nor did it allow a candle to burn in it. He proceeded to reduce the *mercurius precipitatus* without addition, and by this operation he recovered about 8 or 9 cubic inches of oxygen which, when introduced into the mephitic air, made it just like common air. This proved that the calcination of mercury in the air consisted in the combination of a portion of the air with the mercury. He carried out many more experiments on combustion, and was able to prove that in all cases there was a combination of the oxygen with the substance which was burned.

The theory was not quite complete, however. He wanted to find out what happened when inflammable air burned. From the behaviour of various other substances he expected to find an acid, and had searched for it as early as 1774. In 1783, however, he heard of Cavendish's experiments, and together with Laplace (1749-1827) repeated them, and published his conclusions the next day although his results were not sufficiently accurate to warrant his conclusion that "the weight of the water produced could not be other than that of the airs used."

In 1783 the theory of phlogiston was overthrown, and he was able to say, "chemists have turned phlogiston into a vague principle, which consequently adapts itself in all the explanations for which it may be required. Sometimes it has weight, and sometimes it has not, sometimes it is free fire and sometimes it is fire combined with the earthy element; sometimes it passes through the pores of vessels, sometimes these are impervious to it; it explains both causticity and non-causticity, transparency and opacity, colours and their absence. It is a veritable Proteus changing in form at each instant." He renounced phlogiston for "*le principe oxygène*."

As a result of this work Lavoisier formulated more completely the ideas expressed by Boyle about the nature of elements and the function of chemistry. "Chemistry," he writes, "advances to its end by dividing, sub-dividing, and again sub-dividing and we do not know what will be the limits of such operations. We cannot be certain that what we regard as simple to-day is indeed simple, all we can say is that such a substance is the actual term whereat chemical analysis has arrived, and that with our present knowledge we cannot divide it."

Not all the scientists of the age followed Lavoisier in his new theory. Many, including some of the most notable, still persisted in the old errors, but slowly, as young and unprejudiced minds came to study the subject, the new view became accepted.

Lavoisier's experiments have, however, another significance for us, for throughout his work he regards it as axiomatic that "nothing is created, either in the operations of art, or in those of nature," so that in any chemical action, however complicated, no change in the total weight of the

reacting substances takes place. He does not specifically mention this as a deduction from his work, but the whole of his valuable contributions to chemistry are based on the implicit recognition of this principle, which on account of the enormous experimental evidence in its favour has become one of the fundamental generalisations of science. Since Newton's experiments established the proportionality between mass and weight, the principle may be stated as the Law of the Conservation of Mass and may be expressed as follows: "The sum of the masses of all the substances taking part in any (chemical or physical) change is constant." The recognition of this law lies at the root of all quantitative chemistry which would be impossible without it.

Since Lavoisier's time experiments have been made with the deliberate object of testing the validity of the law. The question is of importance, for the measure of the quantity of matter, or mass of a substance, as Newton informs us is its weight, and it is not to be expected *a priori* that the weight of a body, which is not an objective attribute of it should be constant in all circumstances. Bessel (1784-1846) in 1830 by very careful pendulum experiments showed that Newton's result as to the proportionality of mass and weight was correct to 1 part in 60,000, whilst Poynting (1852-1914) and Phillips in 1905 and Southern in 1906 showed that changes in temperature did not alter the weight of a body, whilst Poynting also proved that the weight of a non-isotropic body was independent of its orientation. Very accurate determinations of the weights of reacting substances before and after their reaction were made by Landolt (1831-1910), and others, which established the constancy of mass to an accuracy of 1 in 10,000,000, so that the law is certainly true to the limits of accuracy attainable at the present day.

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CHAPTER IV

THE CORPUSCULAR AND WAVE THEORIES OF LIGHT

THEORIES as to the nature of light have existed from very early times. Owing to the fact that man owes by far the greater portion of his knowledge of the external world to the sense of sight, many of the earliest theories were also largely concerned with vision. At first considerable confusion of thought existed as to whether the emission of light was a property of the body which was seen, or of the eye which observed. Pythagoras (572-497 B.C.), for instance, considered that vision was accomplished by means of particles continuously emitted by a luminous object, which by entering the eye created the sensation of vision. Others, among whom were Plato (*circa* 427-347 B.C.) and his followers, were of opinion that vision was a result of the mixture of something emitted by the eye itself—their “divine fire,” with an emanation from the object. These were supposed to enter into combination with an emanation from the sun, if this was available, and then to return to the eye so that vision resulted. This theory gave an explanation of the fact that vision was not possible in the dark. Aristotle (384-322 B.C.), however, had different views; in his theory light was certainly not a material substance at all, but a quality or action of a medium which he called the “*pellucid*.” In one of his treatises he writes: “Light then is the action of this pellucid, and whenever this pellucidity is present only potentially, there darkness also is present.” Of these theories, that which was formulated by Aristotle in a somewhat vague and fanciful way is the one which has survived in modern theory, though the difference between Aristotle’s quality of a medium and the wave theory of light is extremely great.

In addition to their speculations on the nature of light and vision, the ancients were in possession of a fairly large number of optical facts, some of which played a part in their domestic economy, as is instanced by their use of mirrors and of burning glasses. The simplest two laws of optics, i.e. the rectilinear propagation of light and the equality of the angles of incidence and reflection seem to have been known from the earliest times. The law of refraction, however, proved too difficult of elucidation for them. Ptolemy (A.D. 100-178) tabulated the angles of incidence and refraction in the case of a beam of light passing from air to water, but did not succeed in deducing any law from his observations.

The emission theory in one form or another was the inspiration of all optical thought until it was first seriously questioned in the latter half of the seventeenth century. Various writers, of whom Alhazen (eleventh century), Roger Bacon (1214-1294), and della Porta (1538-1615) were the principal, made important contributions to our knowledge of optics. Alhazen made an anatomical study of the eye and explained the functions of its parts. He believed that vision resulted from emanations of particles from visible objects and showed how the eye received cones of rays proceeding from each point of the object, and not single rays as had been supposed. He also discussed the refraction of the atmosphere and showed how the phenomena of twilight were connected with the height of the atmosphere. Alhazen's work exercised great influence on European thought and was the basis of several commentaries on Optics by Vitellio of Poland (*circa* 1270) and others. Bacon's work has been referred to in Chapter I, and we have seen how he well understood the use of lenses, while his remarkable writings on telescopes and microscopes suggest that he may have been familiar with the actual instruments. Della Porta appeared early in the period characterised by the tendency to dispute the Peripatetic philosophers. His reputation rests mainly on his *Magiae Naturalis* (1558) in which he described the *camera obscura*, spectacles and arrangements of lenses suggestive of the telescope.

In the early years of the seventeenth century the Copernican doctrine regarding the solar system had become gener-

ally accepted. The spread of the new conception created a demand for something better than naked eye observation of the heavens, and so in the early part of the century we find the invention of the telescope in Holland, by Galileo independently in 1610, and its improvement by Kepler. From this time forward there was a continual desire to improve telescopes to assist in the study of astronomy. As magnification increased, the defects of the lenses became more and more apparent. The chief trouble was spherical aberration, though chromatic aberration would begin to be troublesome when the magnification reached about thirty, as it did in Galileo's time.

Many attempts were made to discover the law of refraction so that calculation could assist the makers of instruments in the design of their telescopes. Kepler spent much time in investigating refraction but failed to discover the law. He is credited, however, with twenty-seven empirical rules which were useful in lens making. Kepler had suggested that lenses having the form of surfaces of revolution of the conic sections would get rid of spherical aberration. Descartes demonstrated this mathematically, and lenses were made having these forms but with disappointing results.

James Gregory (1639-1675), in 1663, after coming to the conclusion that chromatic aberration was independent of the figure of the lens, suggested the use of a reflecting telescope as a method of eliminating this trouble. Newton constructed the first reflecting telescope after he had described its principle to the Royal Society on the date of his election thereto.

The correct expression for the law of refraction was obtained about 1621 by Willebrod Snellius (1591-1626), a Dutch astronomer and mathematician, who died without publishing his results. Descartes (1596-1650) published the law to the effect that "if the refracted ray and the incident ray continued through the point of incidence be intercepted by any line parallel to the normal to the surface at the point of incidence, the length of the intercepted portion of the refracted ray is in a constant ratio to the length of the intercepted portion of the incident ray." That is to say, the sine of the angle of incidence bears a constant relation to the sine of the angle of refraction, or

$\sin i / \sin r = \mu$ where μ is the constant which is now called the refractive index.

The next important advance in optics was the discovery of the finite velocity of light. The emission theories had involved the consideration of particles moving with very large velocities which, however, were not specified, whilst Descartes with his fondness for vortex motion had attributed light to a kind of pressure involving rotatory movement, propagated with an infinite velocity in an infinitely elastic medium. Olaus Römer (1644-1710), a Danish astronomer, in 1676, as a result of considerations of the periodic times of Jupiter's satellites, came to the conclusion that light took about eleven minutes to cross the earth's orbit. He noticed that the period of revolution of one of Jupiter's satellites seemed dependent on the relative motion of the earth and Jupiter. If the period were determined when the earth was moving at right angles to a line joining the sun and Jupiter, then this period was larger than when the earth was approaching Jupiter, and less than when it was receding from Jupiter. This could only be interpreted as a consequence of the finite velocity of propagation of light. Römer determined this velocity to be about 190,000 miles per second.

It is worthy of note at this stage that Galileo had tried to measure the velocity of light about eighty years previously, but had failed. The principle of his method was that an observer A should note the time interval between his opening the shutter of a lantern and his seeing the light from B's lantern who opened his as soon as he saw the light from A's. The enormous velocity of light made this method impossible, but the principle served Foucault many years later by the substitution of a mirror in place of the human observer B.

It was about this time that Newton (1642-1727), and Huygens (1629-1695), were simultaneously investigating the problems of optics, and there arose two rival theories concerning the nature of light. These theories divided the scientific world into two groups; one supporting Newton in his theory that light was due to the emission of small particles or corpuscles travelling with enormous velocities in straight lines, and the other Huygens in his theory that light consisted of a wave motion in the æther. The

ether was a necessary postulate of the wave theory as it was considered impossible to have a wave without a medium. The two theories had to explain the then known laws of light. These were (i) its rectilinear propagation; (ii) the law of reflection; and (iii) the law of refraction.

The account of Huygens' theory is given in his *Traité de la Lumière* published in 1690, but written twelve years before. In this work Huygens first gives his reasons for regarding light as being non-material. These are its extremely large velocity of propagation, and the fact that two rays in traversing the same path in contrary directions do not hinder each other, or as he writes, "through the same opening different spectators can see different objects at the same time, and two persons can at the same time see each other's eyes."

He considered each point of a luminous body to be the origin of elementary spherical waves ("though it is not necessary to suppose that the waves are emitted at regular intervals"), the envelope of which at any instant gave the position of the wave-front from the whole body. He then regarded each point on the wave-front as the origin of new elementary waves whose envelope at any subsequent time represented the new position of the wave-front which could be conceived as propagating itself in space in this manner.

This conception of a wave-front as the envelope of an infinite number of elementary waves constituted a great advance in the study of waves. The construction of the wave-front in this way from the elementary or secondary waves is known as Huygens' Construction. Though not free from criticism in the assumptions on which it was founded and applied, it has been of tremendous importance in the solution of all kinds of optical problems.

To explain the rectilinear propagation of light and the formation of shadows, Huygens endowed the secondary waves with the property of being effective only at the points where they touched their common envelope. In these circumstances a sensible disturbance is only found in those places where the elementary waves are touched by the new wave-front, so that in the case of light passing through an aperture the beam will be limited in width by the lines joining the source to the points where the

secondary waves from the extreme portions of the aperture are tangential to the primary wave.

His explanation of reflection is given in Chapter II, "*de la reflexion*," of his book. He considers a portion of a plane wave incident obliquely on a plane surface. One portion of the wave-front will arrive at a point on the plane surface before the rest, so that this point on the surface will then be the origin of a secondary wavelet which will diverge as a sphere in all directions from this point. Immediately this has commenced an adjacent portion of the wave-front will arrive at an adjacent point on the surface, and this point, too, will be the origin of a secondary wavelet diverging as a sphere in all directions. Thus, as successive portions of the wave-front arrive at the surface, consecutive secondary waves are set up from the surface and the envelope of these at any instant, which is the new wave-front, is seen to be turned through an angle such that the perpendiculars to the two wave-fronts before and after reflection make equal angles with the normal to the surface. The perpendiculars to the wave-fronts are what were termed rays by other writers on optics, as they indicate the direction in which the light travels. Thus the law of reflection is easily accounted for on Huygens' theory.

In the case of refraction from a rarer to a denser medium, the treatment is similar except that it is applied to the diverging spherical waves inside the denser medium. Clearly a change of velocity must occur, or the construction would give the same direction in the denser medium as in the rarer, and as it is a matter of observation that the refracted ray is bent towards the normal to the surface, this can only be accounted for if the secondary wavelets set up in the denser medium travel with a smaller velocity than in the rarer one. Thus, the secondary wavelet which starts from the first point of incidence of the wave-front is diverging in the denser medium with a smaller velocity than those in the yet advancing wave, and so the envelope of the wavelets inside the medium is turned through an angle, and the angle which the perpendicular to this wave-front makes with the normal is less than the corresponding angle in the rarer medium. This result that the velocity in the denser medium is less than in the rarer medium is in direct contradiction to the results of any form of emission

theory, and so in later years it became the basis of a crucial experiment to decide between the two theories.

Shortly before this time, in 1670, Erasmus Bartholinus (1625-1698) discovered a few facts in connection with the double refraction of Iceland spar. Huygens repeated his work and gave an explanation in terms of his wave theory. "It was after having explained refraction in ordinary transparent bodies, by the theory of spherical waves of light as above, that I re-examined this crystal, concerning which, I had not been able to discover anything previously." In his chapter "*de l'étrange réfraction du cristal d'islande*" he writes concerning the crystal: "Its transparency is scarcely less than that of water or rock crystal and it is without colour. But rays of light pass through it in quite a different fashion and produce these remarkable refractions. . . . In all other transparent bodies which we know, there is only one simple refraction, but in this substance there are two different ones, so that objects which one sees through it, especially if they are close up against it, appear double, and a ray of sunlight falling on one of its surfaces, divides into two and in this manner crosses the crystal.

"Again, it is a general law in other cases, that the ray which is incident perpendicularly on a surface passes straight through without refraction, and that rays incident at an angle are always refracted. But in this crystal, perpendicular rays suffer refraction and there are rays incident obliquely which pass straight through."

He then described the paths of rays incident in the principal plane of the crystal, and by measurement showed that one of the refracted rays was refracted in the regular way, while the other was refracted in an irregular way, as the ratio of the sines of the angles of incidence and refraction was not constant.

In order to explain these phenomena Huygens made a hypothesis which is best expressed in his own words as follows: "As there were two different refractions, I concluded that there were also two different emanations of light waves, and that one was propagated in the ethereal matter contained in the crystal. This matter being in much greater quantity than the actual particles of which the crystal is composed, was in itself capable of causing the transparency in the way which has been explained

above. I attributed to this emanation of waves, the regular refraction which one observes in this mineral, by supposing that these waves ordinarily have a spherical shape and a smaller velocity inside the crystal than outside it, as I made clear in considering refraction.

“As to the other emanation of waves which should produce the irregular refraction, I wished to determine what would happen with elliptical or rather with spheroidal waves, which I supposed were transmitted by the ethereal matter in the crystal and by the particles of which it is composed, jointly according to the second way in which I explained the phenomenon of transparency.”

Huygens then showed that if the waves in the crystal were spheroidal, a perpendicular beam would be refracted at the surface, but the wave-front would still be parallel to the surface in such a manner that the light would not be transmitted along the lines perpendicular to the waves, as in ordinary refraction, but that the rays would cut the wave-fronts obliquely.

His next step was to find the direction in the crystal which would correspond to the axis of his assumed spheroidal waves. This Huygens did, and showed that it coincided with a certain line of symmetry of the crystal—the optic axis. Having done so much it was a comparatively simple matter to deduce the paths of refracted rays corresponding to any angle of incidence, and Huygens was able to show that his construction and the assumption of spherical and spheroidal waves gave the complete solution.

Huygens also discovered the phenomenon of polarisation but was at a loss to account for it. He took two crystals of Iceland spar and placed them one above the other so that corresponding faces were parallel to each other. A beam of light was incident on the top surface, and of course was refracted into two beams which continued straight through both crystals, the ray due to regular refraction in the first suffering regular refraction in the second, and similarly with the ray due to the irregular refraction. If the crystals were arranged such that none of the faces of the one were parallel to the corresponding faces of the other then each ray from the first crystal was refracted into two rays in the second.

He confessed himself at a loss to account for the first

case where the rays entering the second crystal did not become double, and suggested that in passing through the first crystal they had some new property impressed on them.

Newton's first work in Optics was concerned chiefly with colour. The account of his experiments is to be found in the Philosophical Transactions of the Royal Society for 1672 and in his book on *Opticks*, written in 1675 but not published until 1704, although the results had been communicated to the Royal Society shortly after he was elected a Fellow. Up to this time it was supposed that the colours seen when white light passed through a prism resulted from the mere act of refraction—that each refraction actually produced colour instead of merely separating what were already in existence.

Newton was led to the discovery of the composite character of white light by a series of experiments begun in 1666 in which he passed a beam of light from the sun through a circular opening in a window shutter and then through a prism. He expected to observe a circular patch of illumination on the opposite wall, instead of which he was surprised to find that the coloured spectrum thus produced was about five times as long as it was broad. By placing a second prism close to the first in such a way that the refractions thus produced opposed each other, he observed that the patch of illumination became circular and did not exhibit the coloured effects seen in the former case.

From these experiments Newton concluded that the colours were present originally in the white light of the sun, and that the prism had merely separated them from each other by deviating them through different angles. The results enabled him to establish several propositions regarding rays of light and colour of which the three following are taken from the Philosophical Transactions of 1672 :

- (1) " As the Rays of Light differ in degrees of Refrangibility, so they also differ in their disposition to exhibit this or that particular colour. Colours are not *Qualifications of Light*, derived from Refractions, or Reflections of Natural Bodies (as 'tis generally believed), but *original and connate* properties, which in divers Rays are divers, some

Rays are disposed to exhibit a red colour and no other, some a yellow and no other, and so of the rest. Nor are there only Rays proper and particular to the more eminent colours, but even to all their intermediate gradations.

- (2) "To the same degree of Refrangibility ever belongs the same colour, and to the same colour ever belongs the same Refrangibility.
- (3) "The species of colour, and degree of Refrangibility proper to any particular sort of Rays, is not mutable by Refraction, nor by Reflection from natural bodies, nor by any other cause that I could yet observe. When any one sort of Rays hath been well parted from these of other kinds, it hath afterwards obstinately retained its colour, notwithstanding my utmost endeavours to change it. I have refracted it with Prisms, and reflected it with Bodies, which in Daylight were of other colours; I have intercepted it with the coloured film of Air interceding two compressed plates of glass, transmitted it through coloured Mediums, and through Mediums irradiated with other sorts of Rays . . . but I could never see it change *in specie*."

In this same paper he called attention to the importance of these results in the construction of telescopes, for he writes: "I saw that the perfection of Telescopes was hitherto limited, not so much for want of glasses truly figured according to the prescriptions of Optick Authors (which all men have imagined), as because that Light itself is a Heterogeneous mixture of differently refrangible Rays."

These early researches of Newton on colour led him to investigate more closely other phenomena in which coloured effects were conspicuous and in consequence resulted in his elaboration of the corpuscular or emission theory of light. Before considering Newton's work in this connection it will be useful to consider the emission theory and its explanation of optical phenomena in greater detail.

The rectilinear propagation of light and the formation of shadows followed as an immediate consequence of the law of inertia and consequently presented no difficulties.

In explaining reflection and refraction, however, various postulates regarding the mutual influences of ordinary matter and that of the corpuscles had to be made. Thus in the reflection of light at a surface it was assumed that after travelling in a straight line through an isotropic medium the corpuscles would begin to experience a repulsive action as they approached the surface under consideration. This action would reverse the component of the velocity normal to the surface, at the same time leaving the velocity component parallel to the surface unaltered. Thus any corpuscle incident at an angle to the normal of the surface would leave it at an equal angle on the other side of the normal. In this way the emission theory, on the assumption of a repulsive force acting on the corpuscles in the neighbourhood of a surface, and the laws of collision of perfectly elastic bodies, gave the correct result.

To account for refraction from a rarer to a denser medium it was necessary to assume that when the particle came within a very short distance of the surface it began to be attracted by the denser medium, so that the velocity normal to the surface increased until it penetrated a certain small distance in the new medium, after which it remained constant, while that parallel to the surface was unaltered. This resulted in the velocity of the particle in the second medium being changed in direction and magnitude. Thus if v_1 and i be the velocity and angle of incidence in the first medium, v_2 and r the velocity and angle of refraction in the second, then from the constancy of velocity parallel to the surface

$$v_1 \sin i = v_2 \sin r$$

$$\frac{\sin i}{\sin r} = \frac{v_2}{v_1}.$$

This shows that if i is greater than r , as in the case of light passing from a rare to a denser medium, then v_2 must be greater than v_1 . That is to say, light travels quicker in denser media than in rarer media, so that the velocity of light in matter is greater than its velocity *in vacuo*. This result is in direct contradiction with the corresponding deduction in the case of the theory of Huygens, and later it became the basis of a crucial experiment to decide between the two theories. Its importance was recognised in

Newton's time, but neither he nor his immediate successors were in a position to carry out the experiment.

The fact that reflection and refraction could take place at the same surface proved a great difficulty for the emission theory. Why should some particles be attracted and others be repelled at the same surface? Newton suggested an answer to this question as a result of his experiments on the coloured rings visible round the point of contact of a plane piece of glass and a convex lens. These rings had been noted by Hooke (1635-1703) several years earlier in 1665. Newton's account of the phenomena is given below.

"I took two Object glasses, the one a Plane-convex for a fourteen Foot Telescope, and the other a large double convex for one of about fifty Foot; and upon this laying the other with its plane side downwards, I pressed them slowly together, to make the Colours successively emerge in the middle of the Circles, and then slowly lifted the upper Glass from the lower to make them successively vanish again in the same place. The Colour which by pressing the Glasses together emerged last in the middle of the other Colours, would upon its first appearance look like a Circle of a Colour almost uniform from the circumference to the center, and by compressing the Glasses still more, grow continually broader until a new Colour emerged at its center, and thereby it became a Ring encompassing that new Colour. And by compressing the Glasses still more, the diameter of this ring would increase, and the Breadth of its Orbit or Perimeter decrease until another new Colour emerged in the center of the last: And so on until a third, a fourth, a fifth, and other following new Colours successively emerged there and became Rings encompassing the innermost Colour, and last of which was the black Spot."

Newton then gives the results of his measurements of the rings—their distances apart and also the thicknesses of the layer of air between the glasses corresponding to each ring. He noticed that as the thickness of the air film increased at any point, the colour which was visible there changed, and so made the deduction that in traversing the layer of air the particle which produced that colour had been able to get into a state of easy reflection by the time it reached the second surface and so was copiously reflected. Corre-

sponding to each distance there was then a type of particle which would be easily reflected. For thicknesses of the air layer intermediate between those producing the same colour the reflection was smaller and the transmission greater. In his own words: "Every ray of Light in its passage through any refracting surface is put into a certain transient Constitution or State, which in the progress of the Ray returns at equal Intervals, and disposes the Ray at every return to be easily transmitted through the next refracting Surface, and between the returns to be easily reflected by it.

"This is manifest by the 5th, 9th, 12th, and 15th Observations. For by these Observations it appears that one and the same sort of Rays at equal Angles of incidence of any thin transparent Plate, is alternately reflected and transmitted for many Successions accordingly as the thickness of the Plate increases in arithmetical Progression of the Numbers 0, 1, 2, 3, 4, 5, 6, 7, 8, etc., so that if the first Reflection (that which makes the first or innermost of the Rings or Colours there described) be at the thickness 1, the Rays shall be transmitted at the thicknesses 0, 2, 4, 6, 8, 10, 12, etc., and thereby make the central Spot and Rays of Light which appear by transmission, and be reflected at the thickness 1, 3, 5, 7, 9, 11, etc., and thereby makes the Rings which appear by Reflexion. . . . This alternate Reflexion and Refraction depends on both the Surfaces of every thin Plate because it depends on their distance. . . . It is also influenced by some action or disposition, propagated from the first to the second, because otherwise at the second it would not depend on the first. And this action or disposition, in its propagation, intermits and returns by equal Intervals, because in all its progress it inclines the Ray at one distance from the first Surface to be reflected by the second, at another to be transmitted by it. . . . What kind of action or disposition this is, whether it consists in a circulating or a vibrating motion of the Ray, or of the Medium, or something else, I do not here enquire. Those that are averse from assenting to any new Discoveries, but such as they can explain by an Hypothesis, may for the present suppose, that as Stones by falling upon Water put the Water into an undulating Motion, and all Bodies by percussion excite vibrations in the Air, so the

Rays of Light, by impinging on any refracting or reflecting Surface, excite vibrations in the refracting or reflecting Medium or Substance, and by exciting them agitate the solid parts of the refracting or reflecting Body, and by agitating them cause the Body to grow warm or hot ; that the vibrations thus excited are propagated in the refracting or reflecting Medium or Substance, much after the manner that vibrations are excited in the Air for causing Sound, and move faster than the Rays so, as to overtake them ; and that when any Ray is in that part of the vibration which conspires with its Motion it easily breaks through a refracting Surface, but when it is in the contrary part of the vibration which impedes its Motion it is easily reflected ; and, by consequence that every Ray is successively disposed to be easily reflected, or easily transmitted by every vibration which overtakes it."

The returns of the disposition of any ray to be easily reflected or transmitted were called by Newton its "*Fits*" of easy reflection or transmission.

There is very much in the above which bears considerable resemblance to a wave theory. In fact, Newton did calculate from the diameters of the rings and the thicknesses of the air films, the intervals of the fits. "If the Rays which paint the Colour in the Confine of yellow and orange pass perpendicularly out of any Medium into Air, the Intervals of their Fits of easy Reflection are the $1/89,000$ th part of an Inch. And of the same length are the Intervals of the Fits of easy Transmission." This distance corresponds to half a wave-length which in the yellow-orange portion of the spectrum has a wave-length of about $1/44,500$ th of an inch.

Although Newton argued "the corporeity of light, but without any absolute positiveness, as the word perhaps intimates," he was well aware of the vibratory theory of his "*animadversor*" Hooke, and later of the work of Huygens and its consequences. In Query 28 at the end of his book on *Opticks*, he points out what he considered the greatest difficulty of the wave theory—the rectilinear propagation, for he writes : "If it consisted in Pression or Motion, propagated either in an instant or in time, it would bend into the Shadow. For Pression or Motion cannot be propagated in a Fluid in right Lines beyond an Obstacle

which stops part of the Motion, but will bend and spread every way into the quiescent Medium which lies beyond the Obstacle."

There were, however, phenomena known in Newton's time in which the neighbourhood of the edges of shadows could be seen exhibiting maxima and minima of brightness, both inside and outside the limits of the geometrical shadow. Newton himself devoted much consideration to these effects which he named "*the inflexion of light*," though unfortunately for the development of the subject he was unable to connect it with the consequences he expected from the wave theory.

He describes these effects in the third book of his *Opticks*, and writes concerning them that "Grimaldo has inform'd us, that if a beam of the Sun's Light be let into a dark Room through a very small hole, the Shadows of things in this Light will be larger than they ought to be if the Rays went on by the Bodies in strait Lines and that these Shadows have three parallel Fringes, Bands, or Ranks of colour'd Light adjacent to them. But if the Hole be enlarged the Fringes grow broad and run into one another, so that they cannot be distinguish'd."

Newton's first experiments were merely repetitions of Grimaldi's (1619-1663) which he confirmed and extended. By placing a prism in the beam passing through the hole he showed that if homogeneous light or light of a given colour were used the size of the fringes was such that "those made in red Light were largest, those made in the violet Light were least, and those made in the green were of a middle bigness."

To explain these phenomena Newton supposed the light passing the edges of bodies to be *inflected* by the action of the attractive and repulsive forces active at sensible distances from bodies, and which we have seen were also supposed to be responsible for reflection and refraction. The alterations of brightness and darkness he attributed to alterations of the attractive and repulsive forces, so that "the Rays of Light in passing by the edges and sides of Bodies, (are) bent several times backwards and forwards, with a motion like that of an Eel." The coloured fringes he explained by the assumption that "the Rays which differ in Refrangibility differ also in Inflexibility."

The difficulty regarding rectilinear propagation seems to have been the determining factor in leading Newton to formulate his corpuscular theory, for in Query 29 he writes: "Are not the Rays of Light very small Bodies emitted from shining Substances? For such Bodies will pass through uniform Mediums in right Lines without bending into the Shadow, which is the Nature of the Rays of Light."

He finally disposes of Huygen's theory in Query 26, where he discusses its inability to give a satisfactory account of the double refraction of Iceland Spar: "To explain the unusual Refraction of Island Crystal by Pression or Motion propagated, has not hitherto been attempted (to my knowledge) except by *Huygens*, who for that end supposed two several vibrating mediums within that Crystal. But when he tried the Refractions in two successive pieces of that Crystal, and found them such as mentioned above: He confessed himself at a loss for explaining them. For Pressions or Motions, propagated from a shining Body through an uniform Medium, must be on all sides alike; whereas by those Experiments it appears, that the Rays of Light have different Properties in their different Sides. . . .

"But how two *Æthers* can be diffused through all space, one of which acts upon the other, and by consequence is reacted upon, without retarding, shattering, dispersing and confounding one another's Motions, is inconceivable. And against filling the Heavens with fluid Mediums, unless they be exceeding rare, a great objection arises from the regular and very lasting Motions of the Planets and Comets in all manner of Courses through the Heavens."

It seems a great pity that Newton did not appreciate the wave theory, nor see how it could be modified or regarded so as to comply with the law of rectilinear propagation. It is quite likely also that his attitude and that of his followers was largely though unconsciously influenced by the enormous success with which he had dealt with problems connected with the dynamics of particles, which subject he had placed on a secure foundation, and that these successes prevented them from giving due consideration to the non-material wave theory of Huygens. The necessity for an æther, too, no doubt proved odious to many.

However, Newton decided against the wave theory and

with marvellous sagacity succeeded in making the corpuscular theory explain many phenomena, though in doing so it became necessary to add to the original hypothesis certain features which bear considerable resemblance to a wave theory. Though Newton was proved to be wrong, his emission theory is well worthy of study. In the words of Sir G. G. Stokes: "Surely the subject is of more than purely historical interest. It teaches lessons for our future guidance in the pursuit of truth. It shows us we are not to expect to evolve the system of nature out of the depths of our inner consciousness, but to follow the painstaking inductive method of studying the phenomena presented to us, and to be content to learn new laws and properties of natural objects. It shows that we are not to be disheartened by some preliminary difficulties from giving a patient hearing to a hypothesis of fair promise, assuming of course that those difficulties are not of the nature of contradictions between the results of observations or experiment, and conclusions certainly deducible from the hypothesis on trial. It shows that we are not to attach too great importance to great names, but to investigate in an unbiassed manner the facts which lie open to our examination."

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CHAPTER V

THE ATOMIC THEORY OF MATTER

WE have seen in an earlier chapter that even so long ago as the time of the ancient Greek philosophers two general theories as to the nature of matter were held. One theory maintained that matter was continuous in structure; that however far division and subdivision were carried water was always water, and would always exhibit the properties of water. The facts of nature seemed to accord with this view. It was a matter of common observation, at least so far as could then be ascertained, that the smallest particles which could be abraded from a piece of stone or metal possessed all the characteristics of the original material. However, in spite of the evidence of the senses, Leucippus and Democritus put forward the atomic view to which we have previously referred, and we have seen how they regarded the differences in size and arrangement of the atoms as the causes of the different properties of matter. Under the influence of Aristotle's teaching of a primordial stuff on which the four elements were impressed, this theory languished and practically disappeared.

In more recent times, as more and more properties of bodies became known and investigated, difficulties of explanation were encountered unless some definite structure of matter were assumed. Thus, for instance, when it was considered that air could be so compressed and rarefied that the volume of a given mass of air varied a thousand fold, the idea of a "void" between the particles of matter became insistent. Accordingly Bacon, Hooke, Boyle and Newton as a result of speculations on the nature of heat and the behaviour of gases were led to regard an atomic or particle theory of matter as being more probable than a continuous theory.

So far, however, the idea was merely qualitative and partook more of the nature of a philosophical hypothesis which could not be tested. The first to revive the atomic theory and suggest a quantitative aspect was John Dalton (1766-1844). He seems to have been led to the theory from speculations about the solubilities of gases in water rather than from inductive reasoning based on the results of measurements of the ratios of the quantities of matter involved in chemical combinations, as has been supposed. Since the atomic theory has a very intimate bearing on the nature and mode of chemical combination, it is convenient at this point to devote a little consideration to the ideas on chemical combination prevalent in his time.

A few years previously Lavoisier had established the principle of the conservation of matter, and appears to have considered that the composition of every chemical compound was constant, though Berthollet (1748-1822), a French chemist, in a celebrated controversy (1801-1809) with a fellow-countryman, Joseph Louis Proust (1755-1826), maintained that chemical combination could exist in any proportions, and that cases where a substance of constant composition was obtained were due to the operation of special physical circumstances—such as change in cohesion or solubility of the components. By reference to such cases as are presented by alloys, glasses and solutions, where slight changes in composition produce only slight changes in volume, cohesion, density, etc., Berthollet maintained that the relative quantities of their different components depended only on their mutual capacity for saturating each other. Proust attacked these views in a model of controversy, and by showing that Berthollet was very often dealing with mixtures of different compounds, where of course any proportions of the components could occur, he established the law of constant proportions which the prestige of Berthollet had caused many to doubt. Richter (1762-1807) in his *Rudiments of Stoichiometry, or the Art of Measuring Chemical Elements* (1782-1794), investigated the laws of proportionality between the quantities of bases uniting with a given weight of an acid, and between the quantities of acids uniting with a given weight of a base. He founded his method on the well-known fact of the permanance of neutrality in the double decomposition of

two neutral salts, that is to say, if the acid of one salt is just sufficient to combine with the base of the other, then the remaining acid and base are just sufficient to combine and neutralise each other. From this he calculated that if quantities a and b of two bases are neutralised by a quality c of an acid, then a quantity d of another acid will neutralise both, and conversely, that the weights a and b of two acids which neutralise a given weight c of a base will likewise neutralise a weight d of another base. He drew up a series of tables in which he gave the quantities of analogous compounds (acids or bases) which combine with a given weight of another compound. This work, which later led to the formulation of the Law of Equivalent Proportions, was continued by E. G. Fischer (1754-1831), who also prepared a table, the first table of Equivalents, in which he gave the weights of bases and acids which were equivalent to a standard consisting of a thousand parts of sulphuric acid.

Dalton's views on atoms which were of great utility in explaining the way in which the combination took place were, however, not derived from considerations such as we have mentioned, although they played an important part in providing tests of the theory. The conception in the first place seems to have been purely physical in nature. In his *New System of Chemical Philosophy* (1808), explaining the origin of the theory, he writes that the consideration of the existence of different states of aggregation "led to the conclusion which seems universally adopted, that all bodies of sensible magnitude, whether liquid or solid, are constituted of a vast number of extremely small particles, or atoms of matter bound together by a force of attraction, which is more or less powerful according to circumstances, and which as it endeavours to prevent their separation, is very properly called in that view, attraction of cohesion." He further regarded the particles as possessing a surrounding atmosphere of heat, "a subtile fluid," which prevented them from actually coming into contact.

In a paper written in 1802, but not published until 1805, on *The Absorption of Gases by Water and other Liquids*, he gave the first indication of the quantitative side of the theory. "Why," he writes, "does water not admit its bulk of every kind of gas alike? I am nearly persuaded that the circumstance depends upon the weight and number of the

ultimate particles of the several gases. Those whose particles are lightest and single being least absorbable and the others more according as they increase in weight and complexity. An enquiry into the relative weights of the ultimate particles of bodies is a subject, so far as I know, entirely new. I have lately been prosecuting this enquiry with remarkable success." He then gives his results in which he takes hydrogen as having weight 1, oxygen 5.5, carbon 4.3, nitrogen, 4.2.

Apparently, in order to obtain information on the relative weights of these particles, he had recourse to chemical analysis. By imagining that chemical combination took place in the simplest possible way—an atom of one element joining with an atom of another element and so forming a compound of constant composition, it follows that the relative weights of the components are the same as the relative weights of the atoms. Thus Dalton supposed that in the case of water one atom of hydrogen combined with one atom of oxygen to form one atom of water, and that one atom of nitrogen combined with one atom of hydrogen to form one atom of ammonia. He had no test which would enable him to find out the number of atoms of each element which combined to form an atom of a compound, so he assumed the simplest possible mode of combination.

As a deduction from this visualisation of the mechanism of chemical combination, he was naturally led to the supposition that two elements might form combinations in which there were more than two atoms concerned, and that in consequence there might be types of compounds in which one atom of one element combined with two, three or even more of another. To test this hypothesis Dalton made determinations of the composition of gaseous oxide of carbon (carbon monoxide) and carbonic acid gas (carbon dioxide), and found that if quantities of these gases were taken in which the weight of carbon was the same in each, then the weight of the oxygen combined with the carbon in the case of the dioxide was just twice that in the case of the monoxide. A similar correspondence with his anticipations was found to occur in the analysis of marsh gas (methane) and olefiant gas (ethylene). From these and other experiments Dalton was able in 1804 to propound the Law of Multiple Proportions, to the effect that if two

elements unite to form more than one compound, then if the amount of the one element be constant in the different compounds, the ratios of the amounts of the other element can be expressed by whole numbers. Dalton's theory, which was published in his *New System of Chemical Philosophy*, the first part of which appeared in 1808, met with general recognition in spite of the somewhat arbitrary character of the numbers representing the relative weights of the ultimate particles of bodies, due to his ignorance of the actual number of atoms of the elements in an "atom" of a compound. The theory certainly correlated a large number of phenomena, and probably had quite as much to do with the confounding of Berthollet as the arguments of Proust.

About this time Gay-Lussac (1778-1850) was experimenting with gases, and in consequence of the application of his discovery of the uniform expansion of a gas with temperature, and his knowledge of Boyle's law, he was able to reduce his observations on volumes to standard conditions of temperature and pressure. In 1808 from the results of a number of experiments he asserted that gases always combine together in volumes bearing simple ratios to each other, and that the volume of the resulting product bears a simple ratio to the volumes of the constituents. Thus, for example, he showed that two volumes of hydrogen combined with one volume of oxygen to form two volumes of steam, and that two volumes of nitrous oxide were produced from two volumes of nitrogen and one of oxygen.

In order to bring this result into agreement with the atomic theory it is necessary to deduce from it that equal volumes of gases contain the same number of atoms. Gay-Lussac realised this, and shows at the end of his paper that the similar behaviour of gases to heat and pressure is explicable on the assumption of the same number of atoms in equal volumes of all gases. Dalton, however, would not accept this deduction. In the first part of his *New System* he records his previous speculations on a similar topic. He says there: "In prosecuting my enquiries into the nature of elastic fluids, I soon perceived that it was necessary, if possible, to ascertain whether the atoms or ultimate particles of the different gases are of the same size or volume in like circumstances of temperature and pres-

sure. By the size or volume of an ultimate particle, I mean in this place, the space it occupies in the state of a pure elastic fluid; in this sense the bulk of a particle signifies the bulk of the supposed impenetrable nucleus, together with that of its surrounding repulsive atmosphere of heat. At the time I formed the theory of mixed gases I had a confused idea, as many have, I suppose, at this time, that the particles of elastic fluids are all of the same size; that a given volume of oxygenous gas contains just as many particles as the same volume of hydrogenous."

Consideration of the composition of nitric oxide led him to abandon this idea. If equal volumes of gases contained the same number of atoms, then one volume of nitrogen should combine with one volume of oxygen to form one volume of nitric oxide, whereas it had been shown that two volumes were produced. Hence the nitric oxide contained only half as many atoms as the same volume of nitrogen or oxygen. Thus, there was a real difficulty to prevent Dalton accepting the conclusions of Gay-Lussac.

This difficulty, however, was removed by Avogadro (1776-1856), an Italian physicist, in an *Essay on a Manner of determining the Relative Masses of the Elementary Molecules of Bodies, and the Proportions in which they enter into Compounds*, which was published in 1811. In this essay he modified the Daltonian idea of the ultimate particles of bodies. He seems to have reasoned in this way—that if the atom (*molécule élémentaire*) of oxygen can combine with an atom of nitrogen it might be able to combine with itself and produce a molecule (*molécule intégrante*) of oxygen, and that the combination of nitrogen and oxygen could then be regarded as an exchange of *molécules élémentaires* between *molécules intégrantes*. The following quotation gives very lucidly his own view of the matter: "We suppose, namely, that the constituent molecules of any simple gas whatever (i.e. the molecules of which are at such a distance from each other that they cannot exercise their mutual action) are not formed of a solitary elementary molecule, but are made up of a certain number of these molecules united by attraction to form a single one; and further, that when the molecules of another substance unite with the former to form a compound molecule, the integral molecule which should result splits up into two or

more parts (or integral molecules) composed of half, quarter, etc., the number of elementary molecules going to form the constituent molecule of the first substance, combined with half, quarter, etc., the number of constituent molecules of the second substance that ought to enter into combination with one constituent molecule of the first substance (or, what comes to the same thing, combined with a number equal to this last of half-molecules, quarter-molecules, etc., of the second substance); so that the number of integral molecules of the compound becomes double, quadruple, etc., what it would have been if there had been no splitting up, and exactly what is necessary to satisfy the volume of the resulting gas. Thus, for example, the integral molecule of water will be composed of a half molecule of oxygen with one molecule, or, what is the same thing, two half-molecules of hydrogen."

On this supposition and also of Avogadro's hypothesis that equal volumes of all gases contain an equal number of "*molécules intégrantes*," the reconciliation of the Daltonian theory and Gay-Lussac's observations became possible. For now in the case of nitric oxide a certain number of molecules of nitrogen, each containing two atoms of nitrogen, combine with the same number of molecules of oxygen through an atom of oxygen changing places with an atom of nitrogen in the nitrogen molecule, and the absence of contraction is accounted for. Similar considerations apply to the case of the formation of water (steam) from hydrogen and oxygen—two molecules of hydrogen combining with one molecule of oxygen through each atom of hydrogen taking one of the two atoms of oxygen to itself and so forming two molecules of water.

As a result of this new view of the methods of combination, the numbers which Dalton deduced as the atomic weights of a number of elements required modification. On the assumption that an atom of oxygen united with an atom of hydrogen the atomic weight of oxygen as determined by Dalton was about 7. To be reconciled with the new view of the composition of water this number should be doubled. Similar considerations applied in the cases of carbon, nitrogen, and many other elements. On the assumption of Avogadro's hypothesis it follows that the molecular weights of gases can be deduced from measurement of their densities

relative to the molecule of hydrogen which is taken as 2, so that the molecular weight is twice the vapour density. The application of this theory to many substances did not always give the correct result, so that these ideas did not immediately receive the support of the chemists of that time. The distinction between a molecule and an atom seemed to many to be somewhat arbitrary and unwarranted, and it was long before Avogadro's hypothesis became established as a law, and then mainly as a result of deductions from the kinetic theory of gases, which we shall discuss in a later chapter.

Wollaston (1766-1829), in 1814, advised the rejection of the atomic theory, though he conceded the importance of the numbers given by Dalton as representing the relative atomic weights. He recognised that in chemical combinations, combination took place in proportions governed by these numbers or by multiples of them. Thus the same weights of lead, copper and mercury which combine with 8 parts of oxygen also combine with 16 parts of sulphur, so that in a certain sense 8 parts of oxygen are equivalent to 16 parts of sulphur. Wollaston from considerations of this nature then developed the idea of equivalents as opposed to the physical implications of the atomic theory.

An interesting hypothesis suggested about this time by Prout (1786-1850) became a source of great discussion. The data then available on atomic weights showed that most of them, taken with reference to hydrogen as unity, could be expressed as whole numbers, and this seemed to point to the existence of a primordial form of matter out of which all matter was built up by arrangement. Several chemists took up the problem of determining atomic weights, with a view to substantiating the hypothesis, but Berzelius (1779-1848) and Stas (1813-1891) by means of extremely accurate experiments, showed that the whole number relationship only held very approximately, so that the hypothesis of a primordial matter received no further support on this basis.

The idea of a connection between the different elements, however, still lingered. Many chemists must have wondered if the marked similarity of properties possessed by certain groups of elements, such as chlorine, bromine and iodine and their compounds, had its explanation in some sort of

common origin of the elements. Döbereiner (1780-1849), in 1829, showed that several groups of three analogous elements existed whose atomic weights were such that one was approximately the mean of the other two. J. A. R. Newlands, in 1864, showed that if the elements were arranged in order of atomic weight, every eighth element starting from any one was a kind of repetition of the first. From analogy with an octave in music he enunciated a Law of Octaves which was, however, either ignored or treated with ridicule.

In 1869 Lothar Meyer (1830-1895) and Mendeléef (1834-1907) both showed that there was a connection between the atomic weights and properties of the elements. Meyer showed that by plotting atomic weights as ordinates and atomic volumes as abscissæ, a curve was obtained which exhibited a series of maxima and minima at intervals of eight elements, and that similar elements occupied similar places on the curves. Mendeléef extended the work much further, and showed that if the elements (excluding hydrogen) were arranged in a table in order of their atomic weight, divided into sets of seven and the sets placed under each other, then similar elements were in the same vertical columns and that the chemical and physical properties varied in degree continuously through these columns. In 1871 he was led by certain gaps in the table to prophesy the existence of undiscovered elements whose properties he described. These he called *eka-boron*, *eka-aluminium* and *eka-silicon*, and the discovery of gallium, scandium and germanium in the next fifteen years, which fitted into the gaps in his table, raised the idea of periodicity from the rank of a hypothesis to that of a law of nature, known as the Periodic Law. There are, however, one or two irregularities in the table—thus iodine and tellurium have to be placed in reverse order of atomic weight in order that iodine may come in the same column as chlorine, and tellurium as sulphur. Still the evidence was strongly in favour of the existence of an ultimate interconnection between the various elements, and also of the dependence of the properties of an element on its atomic weight, suggesting that similarity of properties was due to similarity in arrangement of something forming an essential portion of the atom.

One point in connection with the periodic table merits our attention at this point—that is *valency* which may be defined as the property of an element which defines how many atoms of hydrogen one atom of it will either combine with or displace from combination. The variation of the valency is strikingly shown in Mendeléef's table, for all the elements in each vertical column possess the same valency; thus the first column which contains lithium, sodium and potassium, consists of univalent elements which are also the most strongly electro-positive elements (i.e. are liberated in electrolysis with a positive charge so that they are given up at the cathode).

The second column, containing amongst others calcium, strontium and barium, consists of divalent elements which are less electro-positive than those in the first column. Similarly the members of the fourth column are tetravalent and of the sixth column hexavalent, while the electro-positive characteristics have become less and less, fluorine, chlorine, bromine and iodine, members of the seventh column, being very strongly electro-negative.

As a consequence of Rayleigh's (1842-1919) discovery in 1892 of a discrepancy between the densities of nitrogen prepared from the air and from such substances as ammonium nitrate, a new family of elements has been discovered, of which argon and helium are the most important. The determination of γ , the ratio of their specific heats at constant pressure and constant volume, showed that all these elements, which are gases, are monatomic, that is they have zero valency, so that it would be natural to place them in a column to the left of the lithium, sodium family. The values obtained for their atomic weights were also in favour of so placing them in the periodic table, though argon and potassium showed a discrepancy similar to that shown by tellurium and iodine.

The conception of valency has been of great use in chemistry in helping to form ideas as to the structure of compounds, particularly in the realm of organic chemistry where the graphic representation of valency by bonds has led to the development of structural formulæ, without which this branch of science would be almost unintelligible.

The science of the last century was, however, unable to give any account or even plausible theory as to what conditioned the valency of an element, or to determine the manner of the mutual linking of atoms in compounds, since the structural formulæ of organic chemistry only showed which atoms were associated with each other without giving information as to their orientation in space.

We shall see in a later chapter how modern developments have led to important advances in our knowledge of the constitution of atoms, and have given a physical explanation of valency, while the century old speculations of Prout have been revived in a new and more convincing form.

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CHAPTER VI

THE ELASTIC SOLID THEORY OF LIGHT

ALTHOUGH the corpuscular theory light was contested by Franklin (1706-1790), Euler (1707-1783), and a few others during the eighteenth century, the prestige of Newton secured an almost unanimous acceptance for it until early in the nineteenth century, when it was assailed by the brilliant work of Thomas Young (1773-1829). He seems to have been led to his ideas by means of an analogy between light and sound, which he elaborated in a paper read before the Royal Society in 1800. In this paper he discussed the divergence of sound, and suggested that, in the case of light its propagation in the æther in the form of undulations need not necessarily violate the law of rectilinear propagation, and also showed how the composition of sounds took place by means of the superposition of vibrations. He first gave definiteness to these ideas in their application to optics, in his Bakerian Lecture in 1801 on *The Theory of Light and Colours*, which he founded on the following hypotheses:—

1. A luminiferous æther pervades the universe, rare and elastic in a high degree.
2. Undulations are excited in this æther whenever a body becomes luminous.
3. The sensation of different colours depends on the different frequency of vibrations excited by the light in the retina.
4. All material bodies have an attraction for the æthereal medium, by means of which it is accumulated in their substance, and for a small distance round them, in a state of greater density, but not of greater elasticity.

He then developed several propositions, of which number 8 was to the effect that “when two undulations, from different origins coincide either perfectly or very nearly

in the same direction, their joint effect is a combination of the motions belonging to both." He illustrated this principle by reference to beats in the case of sound waves.

In this connection he repeated, with slight modifications, the experiments of Grimaldi already referred to in a previous chapter. When a beam of light is transmitted through two small apertures placed close together, the light diverges from each as from a new source, and on being received by a surface some distance away a series of straight parallel bands showing the colours of the spectrum is seen, each band being separated from the neighbouring ones by regions of comparative darkness. If homogeneous light, say red light, is used, a series of red bands separated by regions of absolute darkness is seen. Young demonstrated that these bands or fringes are due to the mutual action of the beams, for by closing one of the apertures he showed that the fringes disappeared and the dark spaces became bright, thus confirming the astute Grimaldi's statement that an illuminated body may be rendered darker by the *addition of light*. To this effect, which he realised was merely the consequence of the principle of the superposition of small motions, Young gave the name of the interference of light, which although a misnomer in a certain sense, has been retained from his time.

He also investigated the fringes seen at the edges of the shadows of narrow objects, and applied the wave theory to their elucidation. In this case there are two sets of fringes, one exterior, and the other interior, to the geometrical limits of the shadow. Newton only mentions the exterior set, and appears to have overlooked the other, which were, however, described by Grimaldi. The exterior fringes Young attributed to the interference of two portions of light, one of which passed by the edge of the body and was more or less inflected, while the other was obliquely reflected from the edge. The interior ones he attributed to the interference of the inflected waves passing near to the two edges of the body. That this was correct he showed by placing an opaque screen to intercept the light passing by one side, with the result that the interior bands immediately disappeared, although the light passing the other side was unaffected. As regards the fact of inflection itself,

he considered that this was due to refraction in the æthereal layer of varying density which he assumed to exist in the neighbourhood of bodies, though later he was led to modify this view and to ascribe the cause to a fundamental property of waves.

Young also applied the wave theory to the explanation of Newton's rings, and proved that the phenomena of the reflected rings could be deduced very simply from the principle of the interference of the light reflected from the two surfaces of the air film. In addition, he showed that the states of the two interfering beams was not that deduced from the geometrical difference in path, but that one of them had undergone a change of phase at the instant of reflection which was equivalent to an increase in path amounting to one-half an undulation. He pointed out that the two reflections occur under different conditions, one beam being reflected at a rarer and the other at a denser medium, and that the direction of vibratory motion of the undulations must be reversed in one case and not in the other. This principle he put to the test in a most remarkable experiment. We have seen in discussing the work of Newton, that when the air film is extremely thin, there is a black spot at the centre of the ring system. In this case the air film is so thin that the whole difference of path is that due to the loss of half an undulation by one beam, which, when combined with the other, produces darkness. It followed from Young's reasoning that if the film were of optical density (i.e. refractive index), intermediate between those of the media between which it was situated, this loss of half an undulation would not occur and the centre of the ring system should be white. By substituting oil of sassafras for air, Young had the satisfaction of confirming this brilliant prediction.

So far the undulatory theory had been wholly descriptive. By calculating the differences in path traversed by two rays when they interfered, Young made a very important quantitative contribution to the theory. These differences, he found, formed an arithmetical progression if calculated for any homogeneous light, and that the common difference varied and depended on the colour of the light used, being greatest for red light and least for blue. As a result of these experiments he was able to

formulate a new "simple and general law" in 1802 to the effect that "whenever two portions of the same light arrive at the eye by different routes, either exactly or very nearly in the same direction, the light becomes most intense where the difference of the routes is a multiple of a certain length, and least intense in the intermediate state of the interfering portions; and this length is different for light of different colours."

This length is, of course, identified with what is called the wave-length of light, that is, the distance in a train of waves at which the character of the displacement constituting the vibration repeats itself. In the case of red light Young found that the wave-length was about 0.00007 cm., while for blue light it was about 0.00004 cm. The same values for the wave-length were obtained by Young from calculations based on the two apertures and on the diameters of Newton's rings, so that he was justified in concluding that these apparently different phenomena could be referred to one principle.

The work of Young, however, did not at first receive serious consideration from his scientific contemporaries, so that it was not until about fifteen years later when Augustin Jean Fresnel (1788-1827) commenced his investigations that the undulatory theory of light received the attention of the scientific world. From a consideration of the fringes seen in the shadow of small opaque objects Fresnel had discovered the principle of interference for himself. At first he attributed the external fringes to the interference of the direct and reflected light from the edges, but gave this theory up when he found that the intensity of the fringes was independent of the shape of the edges.

Meanwhile a new impetus to investigation was provided by the phenomenon of the polarisation of light. The polarisation observed by Huygens had remained an isolated fact for more than a hundred years, until Malus (1775-1812) in 1808 rediscovered it in the case of light reflected from the surface of transparent substances, thus providing a convenient means of isolating polarised light. Great interest was aroused by this new phenomenon, and at once a host of investigators commenced the study of the properties of the new kind of light, among whom were Arago, Brewster, Biot, Poisson and Young. Arago (1786-

1853) showed that at all angles of incidence the reflected and refracted beams contained equal portions of polarised light, while Brewster (1781-1868), in 1815, showed the angle of polarisation varied with different substances and discovered the law which bears his name, to the effect that the tangent of the polarising angle is equal to the refractive index of the substance.

Biot (1774-1862), who was a strong supporter of the corpuscular theory, investigated the colours of thin crystalline plates. These colours are seen if light polarised by reflection at the polarising angle from a surface is transmitted through a thin crystalline plate and afterwards reflected from another plate at the polarising angle so that the second plane of incidence is perpendicular to the first. Young attributed the coloured effects to the interference of the two beams of light produced in the doubly refracting crystal, which he considered were in a condition to interfere. But a serious difficulty arose here. It was difficult to see why the colours should not be visible in ordinary light since this is broken up into two portions in passing through a doubly refracting crystal. It occurred to Fresnel and Arago in 1816 to investigate the conditions under which two beams of polarised light can interfere, and as a result they solved the difficulty and formulated the laws of the interference of light. They found that two rays of light polarised in the same plane, interfere under the same circumstances as two rays of ordinary light; that when the planes of polarisation are inclined the interference is diminished; and that when the angle between the planes is 90° they do not interfere at all.

Hence the two rays which emerge from the plate cannot interfere until their polarisations are made the same by reflection from the second reflector. As a result of these experiments, Young, in a letter to Fresnel early in 1817, suggested that the peculiarity of waves which gave rise to polarisation might be due to the direction in which the motion took place, and that the displacement was possibly transversal and not longitudinal as had hitherto been contemplated in the study of waves.

Young's suggestion of transverse waves was at once accepted by Fresnel. He had considered it previously, but had not managed at the time to reconcile the hypotheses

with the principles of mechanics. The æther had been considered as *an elastic fluid*, so that the only vibrations it could transmit were of necessity supposed to be longitudinal, whereas transverse waves necessitate rigidity in the medium transmitting them, which thus would appear to have the properties of *an elastic solid*. The hypothesis was soon afterwards shown to be a consequence of the laws of the interference of polarised light on any wave theory, for the experiments of Fresnel and Arago on the non-interference of two beams polarised at right angles to each other could only be reconciled with a wave theory if there were no longitudinal components in the vibrations at all. Thus the phenomenon of polarisation was simply due to the resolution of transverse vibrations into two sets in which the displacements constituting the vibrations were at right angles.

The wave theory of light so far had not been accepted with anything like unanimity. Scientists were still divided into two parties, each claiming great intellects, which battled for either the corpuscular or the wave theory. Further division was created by the notion of transverse vibrations. Many who were ardent supporters of the new theories could not reconcile themselves to the idea of a wave motion in which the displacements were anything but parallel to the direction of propagation. Among these was Poisson (1781-1840) who, while doing so much to support the general wave theory, refused to accept the possibility of transverse vibrations, even up to the time of his death.

In his celebrated *Mémoire sur la Diffraction de la Lumière* of 1818, Fresnel laid down the laws of diffraction and based them on the principle of Huygens and the principle of Interference. In applying these principles he supposed the wave surface to be subdivided into an indefinite number of equal annular portions and applied the principle of interference to determine the resultant effect at any point due to all the elementary waves sent out by them. This resultant is given in terms of two integrals, which, when evaluated for the particular boundary conditions of the problem, give the illumination at any point. The result for points in the neighbourhood of geometric shadows exhibits maxima and minima corresponding to the fringes seen at the edges of shadows.

The comparison of the results of the theory and experiment led to remarkable agreement of the two, while Poisson, applying the same principles, deduced the surprising result that the illumination in the centre of the shadow of a circular disc is exactly the same as if there were no disc at all—a result which was confirmed in all respects by Arago.

Fresnel now set himself the task of bringing order into all the exceedingly complicated phenomena of polarisation, double refraction and the colours of crystalline plates. In 1821 he solved the problem of the reflection of light. In doing this he was led to make certain assumptions with regard to the state of the æther in different bodies. Now the velocity of propagation of waves in the æther or in any other medium, depends on the ratio of the elasticity of the medium to its density. Fresnel assumed that the elasticity of the æther was the same in all media and that its density varied in different media. The wave theory suggested that the velocity of light in material substances was less than that *in vacuo*, as did also the movements of the fringes in Fresnel's modification of Young's experiment with two apertures, when a plate of glass was placed over one of them, though this could not be regarded as a definite proof. Thus the supposition of variable density was the simplest supposition which would make the ratio of elasticity to density of the æther less in ponderable bodies than *in vacuo*. From these hypotheses and the assumption that there was no loss of *vis viva* (or energy, as Young suggested as the name for one-half of this quantity) he deduced the intensity of the reflected light, for light polarised in, and parallel to the plane of incidence, and also obtained Brewster's Law.

Very little progress had been made in explaining double refraction from the time of Huygens until Fresnel attacked the problem and produced a theory which was probably the greatest scientific achievement since the time of Newton. We have seen how Huygens, to account for the existence of double refraction in Iceland spar, was led to the assumption that there were two vibrating systems concerned—one the æther propagating the spherical waves, and the other the crystal and æther jointly propagating the spheroidal waves. Instead of assuming two media Fresnel based his work on the assumption that the rigidity of the æther in

a crystal is different in different directions. Since the velocity of vibrations in elastic media is proportional to the square root of the elasticity, a surface can be drawn in the crystal with any point as origin, such that the *radii vectores* from the origin to any point on the surface are proportional to the square roots of the elasticity in those directions. This surface he called the surface of elasticity. The velocity of propagation in any direction being thus known from the surface of elasticity, Fresnel calculated the form of the wave surface—the surface which is tangential to an indefinite number of plane waves all of which commence at the origin, and found it to be a complicated surface of the fourth order from which, if the elasticity is symmetrical about an axis, Huygens' spheroid can be deduced, while if the elasticity is equal in all directions the wave surface becomes a sphere.

The work of Fresnel thus placed the wave theory of light on a firm foundation. As Herschel, in 1833, writes: "Fresnel succeeded in erecting a theory of polarisation and double refraction, so happy in its adaptation to facts, and in the coincidence with experience of results deduced from it by the most intricate analysis, that it is difficult to conceive it unfounded. If it be so, it is at least the most curiously artificial system that science has yet witnessed; and whether it be so or not, so long as it serves to group together in one comprehensive point of view a mass of facts almost infinite in number and variety, to reason from one to another, and to establish analogies and relations between them, on whatever hypothesis it may be founded, or whatever arbitrary assumptions it may make, it can never be regarded as other than a most real and important accession to our knowledge."

The work of Young and Fresnel by the time of the latter's early death in 1827 had given a kinematical explanation of the propagation of light waves. The work of their immediate successors was the establishment of the theory on sound dynamical reasoning. This work led to the development of the Elastic Solid Theory of Light which we shall now briefly review.

The elastic solid theory of light arose out of the attempts to provide a dynamical basis for the phenomena of light conceived as a transverse vibratory motion in what was

called the luminiferous æther. The somewhat analogous problem in the case of the longitudinal vibrations constituting sound had been fairly satisfactorily dealt with by Newton, his successors, and finally by Laplace and Poisson. In this case it was known that the propagation of the wave was due to the forces of restitution brought into play by the successive condensations and rarefactions in the medium, and that the velocity of propagation was proportional to the square root of the ratio of the elasticity of volume to the density of the medium.

Poisson had shown that an arbitrary disturbance produced in a solid body would give rise to two sets of wave motions which would, in general, be propagated with different velocities. He also proved that whatever the character of the initial disturbance the vibrations in one set of waves would be longitudinal and in the other transversal to the rays, and that the former were of the same type as the waves propagated by fluids, while the latter were propagated with a velocity dependent on the resistance to distortion of the medium.

Now fluids offer no resistance to distortion, and hence cannot transmit transverse vibrations, so that the postulation of vibrations of this type is equivalent to endowing the æther with the properties of a solid in opposition to the conception of it as a perfect fluid, as was suggested by the unresisted motion of the planets through it. It was immediately seen that such an æther should propagate two kinds of wave motions, one which could be identified as light and the other longitudinal, which could not be accounted for, though various hypotheses were made on more or less plausible grounds to explain its absence.

With regard to this difficulty Stokes makes the following remark, which indicates clearly the fundamental assumptions of the theory: "Suppose a small quantity of glue dissolved in a little water so as to form a stiff jelly. This forms in fact an elastic solid. It may be constrained, and will resist constraint and will return to its original form when the constraint is removed, by virtue of its elasticity; if constrained too much it will break. Suppose the quantity of water in which the glue is dissolved is gradually increased until it is only glue water. At last, it will be so far fluid as to mend itself, as soon as it is dislocated. Yet, there

seems hardly sufficient reason to suppose that at a certain stage in the dilution, the tangential force whereby it resists constraint, ceases all of a sudden. In order that the medium should not be dislocated and therefore should have to be treated as an elastic solid, it is only necessary that the amount of constraint should be very small. The medium would however be what we should call a fluid as regards the motion of normal bodies through it. The velocity of propagation of normal vibrations in our medium will be nearly the same as that of sound in water; the velocity of propagation of transverse vibrations depending as it does on the tangential elasticity will become very small. Conceive now a medium having similar properties, but incomparably rarer than air, and we have a medium such as we conceive ether to be—a fluid as regards the motion of the earth through it, an elastic solid as regards the small vibrations which constitute light. The sluggish transverse vibrations of our jelly are in the case of the ether replaced by vibrations propagated with a velocity of nearly 200,000 miles per second. We should expect *a priori* the velocity of propagation of normal vibrations to be incomparably greater.”

In the hands of Neumann (1798-1895), MacCullagh (1809-1847) and particularly Green (1793-1841) and Stokes (1819-1903), the theory was developed so that it gave fair agreement with most of the phenomena by which it could be tested, though no form of it could claim freedom from doubtful assumptions or even the prediction of results contrary to those of experience. The various modifications in the theory were usually tested by their ability to give the reflection formulæ obtained by Fresnel, which had been verified by Brewster, the wave surface in crystals and the law of polarisation by reflection.

In addition to the difficulty of the postulate regarding the possession by the æther of something analogous to rigidity, the theory experienced difficulty in framing consistent assumptions as to the state of the æther in ponderable bodies. The fact that light can travel through a vacuum as, for instance, interstellar space, had led to the idea that even in ponderable bodies light was still transmitted by the æther, though it might be modified by the presence of matter. Consequently in order to account for

the smaller velocity of light in matter than *in vacuo* two assumptions regarding the state of the æther became possible. The first of these, which we have seen was adopted by Fresnel, was that the rigidity of the æther was everywhere the same, but that its density varied in different media, so that the velocity of propagation of light varied inversely as the square root of the density of the medium. MacCullagh, on the contrary, assumed that the change of velocity was a result of the change in the rigidity of the æther in different media. Unfortunately, the optical phenomena could be fairly well explained on either hypothesis. As regards the condensational wave there was in most cases a tendency to ignore it. If the æther were incompressible the velocity of this wave would be infinite, while Lord Kelvin (1824-1907) showed that it was equally consistent to assume that this velocity was infinitely small.

Fresnel's formulæ for the intensity of a ray reflected from a transparent body was shown to be sound only on the supposition of variable density and it also implied that the vibration was perpendicular to the plane of polarisation, but the investigation of the law of double refraction in crystals by Green, in which the further postulate was made that for crystals, the optical elasticity as well as the mechanical elasticity was different in different directions, forced one to the opposite conclusion.

One definite fact, however, did emerge about this period which had an important effect, inasmuch as it finally disposed of the emission theory. We have seen that the two theories differed fundamentally in attributing different velocities to light in material media, the emission theory indicating a velocity greater than that *in vacuo* while the wave theory led to the contrary conclusion. In the development of the wave theory by Fresnel and others, some evidence accumulated supporting this conclusion, such as the shift of the interference bands in Young's arrangement when a plate of glass was interposed in one of the interfering beams. The crucial experiment was that of the direct determination of the velocity of light in different substances. It was not until 1850, however, that this experiment was made, when Foucault (1819-1868), using a method suggested by Arago in 1842 involving the use of a revolving mirror, determined the velocity of light in both air and

water. The principle of the experiment consisted in measuring the angular shift of the revolving mirror in the time interval between the instant of reflection of a beam of light, and that of its return after travelling to a fixed mirror whence it was reflected back to the revolving mirror. Though the quantities to be measured were extremely small, the result was unmistakably in favour of the wave theory, and the velocity of light was shown to be inversely proportional to the refractive index of the medium.

All attempts at the construction of a strictly elastic solid theory were attended with inconsistencies such as have been mentioned above. It is obvious that such theories could not account for all the phenomena, as dispersion, absorption and fluorescence, received no explanation at all on such theories. The evidence of eclipses and all astronomical observations was to the effect that light of all wave-lengths travelled with the same velocity *in vacuo*, while the different refrangibility of different wave-lengths in material media showed that in these cases the velocity depended on the wave-length. To bring these facts into any theory of light, postulates regarding the interconnection of matter and æther were necessary in addition to those respecting the density or rigidity of the æther in such matter.

Cauchy (1789-1857), in 1835, brought forward the idea that in material media the æther was distributed round the molecules in shells of varying density, and that the distance apart of the molecules was small compared with the wave-length of light. He then obtained a relation between the refractive index and the wave-length, which agreed with experiment in the visible spectrum, but differed considerably from observations in the infra-red region. Maxwell (1831-1879), in 1869, and later Sellmeier and others, developed the idea that the molecules of material media were, so to speak, embedded in the æther and that their displacement brought into play forces of restitution. On the assumption, then, that the æther in dispersive media was loaded with molecules which were free to perform forced vibrations of the same period as that of the transmitted light, Sellmeier showed that the velocity of propagation is greatly increased if the frequency of the light wave is slightly greater, and greatly diminished if it is slightly less than the natural period of the molecules, and

so gave a dynamical explanation of the so-called "anomalous dispersion" which was discovered about 1860. Helmholtz, working on similar lines, introduced a frictional term and obtained formulæ connecting wave-length and refractive index, which also accounted for absorption and gave excellent agreement with experiment over large regions of the spectrum.

In spite of the difficulties inherent in the elastic solid theory, these were not, as a rule, considered fatal to the theory which was believed, mainly on account of its successes, to give a fair presentation of the facts. Progress was next made as a result of the wider philosophic outlook bequeathed to the scientific world by Maxwell in the ideas which ultimately led to the electromagnetic theory of light. This is discussed in greater detail in Chapter VII, but deserves notice here on account of the revolution it created in the point of view of regarding the ultimate character of optical phenomena.

We have seen that for the propagation of light the existence of a universal æther had been assumed. A similar universal *plenum* was at the same time regarded as the vehicle of electromagnetic phenomena. It was known, of course, that each involved the propagation of effects with a large known velocity in the case of light, and with a large unknown, and possibly infinite, velocity in the case of electromagnetism. Apart from the discovery by Faraday that the plane of polarisation of light was changed by reflection from a magnet, there was no definite suggestion of any fundamental interconnection between the two sciences.

Maxwell, prejudiced against the notion of two media coexisting and completely filling space, enquired into the properties of the medium in which electromagnetic effects took place, and as a result showed that such effects should be propagated with a definite velocity. This velocity, which he showed could be deduced from the comparison of the unit of electric charge expressed in two systems of units—the electrostatic and electromagnetic systems, turned out to be the same as that of light *in vacuo*. Thus any medium which explained electromagnetic effects might possibly explain optical phenomena. The genius of Maxwell then developed the electromagnetic theory of light in which heat radiation, light radiation, and electromagnetic

radiation (then only predicted, but discovered in 1887 by Hertz) were all considered to be of the same nature, differing merely in the magnitude of the wave-lengths considered and involving the use of different instruments for their detection—thermopiles, for instance, for heat radiation, the retina for light radiation, and the photographic plate or photo-electric cell for ultra-violet radiation.

Many of the difficulties attendant on the old elastic solid theory here found their solution. In Maxwell's theory there was no room for a longitudinal disturbance, and consequently no necessity for the various artifices which had formerly been suggested to suppress it, while the conflicting evidence as to the direction of the vibration with respect to the plane of polarisation was accounted for by the presence of vibrations both parallel to and perpendicular to the plane of polarisation. Electric induction or polarisation became identified with the mechanical displacement of Fresnel, while magnetic induction took the place of the mechanical displacement of Neumann and MacCullagh.

Maxwell's theory was mainly mathematical, and he was unable to give any account of the nature of the electromagnetic vibrations. Objections to the theory were made by Kelvin who, in 1884, in his Baltimore Lectures on the Wave Theory of Light dismissed the electromagnetic theory from consideration as being inadmissible and undynamical, mainly on account of the vagueness associated with the character of the "displacement." He modified his views in favour of the theory on the publication of the lectures in 1904, as many of the predictions of Maxwell had by that time been verified, but he was never convinced of the complete adequacy of the theory as were almost all the rest of the scientific world by that date.

The difficulties which exist even to-day are pointed out by Mallik in his *Optical Theories* (1917), in the following quotation: "The theory, however, is capable of fairly satisfactorily explaining most of the phenomena of optics. But the outstanding questions remain—what is the intimate nature of the medium that is the seat of electromagnetic phenomena, and what is the intimate nature of electricity and magnetism, of electric displacement and electric and magnetic stress? Optical effects are certainly due to

periodic changes of some properties of a medium, which we call the ether. The direction of propagation of this change is the direction of the flow of energy in the medium. But of the intimate nature of the mechanism by which this energy is produced or redistributed and propagated, we have no knowledge."

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CHAPTER VII

MAGNETISM AND ELECTRICITY

THE facts that rubbed amber will attract light bodies such as chaff, and that a naturally occurring mineral—the lodestone—will attract iron, seem to have been common knowledge since very early times. Thales of Miletus (*circa* 585 B.C.) appears to be the earliest philosopher of whose reasoned opinions concerning these phenomena we have any account. Contrary to previous ideas, which had attributed a supernatural origin to these effects, Thales seems to have believed the attraction to be a natural property of the lodestone and the amber. “Thales too,” writes Aristotle, “as is related, seems to regard the soul as somehow producing motion, for he said the stone has a soul since it moves iron.”

No further knowledge regarding the peculiar properties of amber seems to have been obtained until the sixteenth century. In the case of the lodestone, however, a gradual increase of knowledge of its properties is to be recorded. The fact that the lodestone or magnet can give to pieces of iron in contact with it, the similar property of attracting other pieces of iron was well known in the time of Plato (*circa* 427-347 B.C.), who quotes Socrates as saying “For that stone (*viz.* the lodestone) not only attracts iron rings, but also imparts to them the similar power of attracting other rings; and sometimes you may see a number of pieces of iron and rings suspended from one another, so as to form quite a long chain and all these derive their powers of suspension from the original stone.” Lucretius (*circa* 98-55 B.C.) in his poem *De Rerum Natura*, three centuries later refers to the same property of the lodestone. Up to his time all references to the phenomena were concerned with the attraction of the iron for the lodestone, the repulsion which

would occur if two magnets had their similar poles together does not appear to have been recognised before. "Sometimes, too," writes Lucretius, "it happens that the nature of iron is repelled from this stone being in the habit of flying from and following it in turns." He also noticed with surprise—a surprise which was shared by all natural philosophers down to the nineteenth century, that iron filings "will rave within brass basins" if the stone is moved underneath.

St. Augustine (354-430), too, described the same phenomenon and wrote that on seeing it for the first time he was thunderstruck. He was puzzled why the lodestone refused to move straws and yet snatched the iron, and seems to be the first to have realised that the amber and lodestone attractions are manifestations of different properties.

Although so very little was known of the lodestone there was early recognised one property of it which in its application to human life contributed very greatly to the progress of civilisation. This property is the property of a freely suspended or floated lodestone, of coming to rest in an approximate north and south line, and the application is in the mariner's compass. Who first discovered this property, and who first applied it are questions which cannot with surety be answered. The credit is claimed for many peoples—the Greeks, Phœnicians, Chinese and the Arabians. It is sufficient here to state that the earliest European reference to the mariner's compass occurs in the works of Alexander Neckam (1157-1217), one of the English Schoolmen, in his book, *De Utensilibus*: "If then one wishes a ship well provided with all things," he writes, "one must have also a needle mounted on a dart. The needle will be oscillated and turn until the point of the needle directs itself to the North, thus making known to the sailors the route which they should hold while the Little Bear is concealed from them by the vicissitudes of the atmosphere."

We must now consider the work of a very remarkable person in the history of magnetism—Master Peter de Maricourt, or, as he is usually called, Peter Peregrinus (thirteenth century). His experiments on magnetism are described in a letter written from the trenches before

Lucera, in 1269, to a friend, Sigerus of Foucaucourt, his neighbour at home. It is written as if in answer to queries from Sigerus regarding magnets, the properties of which are discussed as a preliminary to make clear the working of a machine giving perpetual motion.

Early in the letter he writes of his discovery and differentiation of the poles of a magnet, and shows how they may be determined in the case of a globular lodestone by noting the direction taken up by needles when placed on the lodestone. All these directions "will run together in two points just as all the meridian circles of the world run together in two opposite poles of the world." He notices that at these points the needles are most attracted by the lodestone, and also that at these points they stand out perpendicularly to the lodestone, which fact also gives another method of finding the poles.

He then shows how the poles may be distinguished from each other. "Take a wooden vessel, round, like a dish or platter and put the stone in it . . . then put this in a larger vessel containing water, so that the stone may float like a sailor in a boat. . . . Since the north and south parts of the heavens are known, so will they be known to the stone, because each part of the stone will turn itself to its corresponding part of the heavens."

The next step he takes now that the poles are differentiated from each other is to find the effect of a north pole on a south pole. He suggests the use of two lodestones with their poles marked by cuts: "If the north part of the stone, which you hold, be brought to the south part of the stone floating in the vessel, the floating stone will follow the stone you hold, as if wishing to adhere to it. . . . Know it therefore as a law that the north part of one stone attracts the south part of another stone, and the south, the north."

In addition to the discoveries in this important series of experiments he also showed that the poles of a weak magnet could be reversed by the action of a stronger one, and that each of the pieces into which a magnet is broken, is a complete magnet itself. He also made several improvements in the compass by adding to it a scale and a fiducial line, so that it could be used directly for steering instead of merely indicating the direction of the North Star.

The results of his work, however, were soon forgotten, for although a few manuscript copies of the letter were made they do not seem to have fallen into the possession of anyone who could make use until about 300 years afterwards, when William Gilbert (1540-1603) reviewed the whole of the known work on the subject in his book *De Magnete* (1600), where he exposes the errors of the earlier philosophers, makes clear and definite knowledge already existing, and adds the results of his own experiments. Gilbert's work was characterised by precise observation, the experiments described in his book were, he avers, "all of them done again and again under my own eyes." His object in writing the book was to provide a physical basis for the heliocentric idea of the solar system put forward by Copernicus in 1543, to which Gilbert was the first English convert. His main discovery in magnetism was that the earth was magnetic. This he demonstrated from his experiments on a "*terrella*"—a globular lodestone similar to that of Peter Peregrinus. Whereas Peregrinus had regarded his lodestone as being a model of the heavens and had likened its poles to the poles of the sky, Gilbert regarded it as a model of the earth. Peregrinus considered that the compass was acted upon by the poles of the heavens represented by his model; Gilbert by the actual poles of the earth represented by his "*terrella*." In support of this he showed that iron can be magnetised by being placed in the meridian, particularly if it be heated while in that position, and thus explained the magnetisation of iron rods taken from churches in which they had lain in a north and south position for many years.

In common with the majority of the natural philosophers of his time, he attempted to make his magnetic discoveries the basis of a system of cosmogony in which he evolved a theory of exhalations and magnetic orbs of virtue extending, in the case of the earth, as far as the moon, and so producing irregularities in its motion which he endeavoured to explain.

He then turned his attention to the amber attraction, which was universally considered to be of the same nature as the lodestone attraction. What puzzled him most was the directive capacity—the "verticity," as he called it—of the lodestone which was absent in the amber. As a

result of his experiments he was able to state: "For not only amber and jet, as they (viz. certain Italian physicists) think, attract corpuscles, but so also do the diamond and sapphire, glass, sulphur, hard resin and rock alum." In investigating these materials he used the first electrical instrument—a light metal rod poised centrally on a point, which he called a "*versorium*" and which nowadays would be called an electroscope. It turned to rubbed materials if they exhibited the attractive effect.

Gilbert immediately recognised that he had discovered a new property of matter. The mysterious amber was not alone in its possession of this property, so he gave the general name of "electrics" to all these substances. He had definite ideas on the differences between magnetism and electricity, and was of opinion that in magnetism the attractive force was towards arrangement and order, whilst in electricity it was towards building up and binding together the small parts of bodies. He did not get very much further in his electrical experiments, however. Though his experiments often resulted in discoveries, yet in his conclusions and deductions from them he was often very much in error.

Nearly all physicists of the century succeeding Gilbert examined the phenomena presented by the lodestone and the amber, but no one for some time made a really great step in the advancement of knowledge on the subject. Progress was indicated by the announcement of the more or less isolated discoveries which are rapidly surveyed below.

Cabaeus (1585-1650) about 1629 discovered that when an electric attracted small particles, after a few moments, instead of merely falling off they were very often repelled from the electric. He was unable to account for this though his theory of electric action attempted an explanation of it.

Von Guericke (1602-1686) constructed an electric "*terrella*" of sulphur with which he made experiments on attractions. The electrification of the sulphur ball was accomplished by stroking with the dry palm. He also noticed that if it were rubbed in the dark "light will result, as when sugar is beaten." He regarded his "*terrella*" as a model of the earth in which electrification by the

friction of the sun's rays took the place of rubbing with the dry palm.

Stephen Gray (1696-1736) enquired whether the virtue which the amber got by rubbing could be conveyed to other bodies. With this object he rubbed a long tube with a piece of cork in one end, and found that light articles flew as readily to that as to the glass, so that the virtue had passed from the glass to the cork. He then tried to find how far it would travel, and so inserted into the cork a wooden rod 4 inches long with an ivory ball at the end of it, and still found that the virtue travelled to the ball. He then used his fishing-rod and fastened other rods to it, and the virtue still travelled to the end of them. In 1729 he visited a friend and showed him the experiment. The friend immediately wanted to put up a long line and investigate. This they did, and as Gray apparently had found out previously that he could keep his charges better if they were suspended by thin threads, they suspended a line along a gallery 80 feet long, supporting it at intervals by thin tight silk threads across the gallery, and passing the line backwards and forwards across the silk until it was over 300 feet long, and still the virtue seemed to experience no difficulty in travelling. Then the silk threads broke under the weight. It was an easy matter for them to be replaced, so this time they substituted stronger metal wires for the silk, but now they got no results at the end of the line no matter how strongly they rubbed the tube at one end. They were very puzzled, but happily an explanation occurred to them: "We are now convinced," writes Gray, "that the success we had before, depended on the lines that supported the line of communication being silk, and not upon their being small." Gray and his friend had discovered that certain substances would conduct electricity and that others would not. They then erected a land line on poles for 650 feet and got effects transmitted from one end to the other, until in the evening when the dew fell, the effects suddenly stopped, though Gray was not positive that the dew was responsible, as he says he had become very hot with excitement and running from one end of the line to the other, and that might have been the cause. So he left his friend electrifying "a hot poker, a live chicken, a large map, and an umbrella,"

and returned to the Charterhouse where he continued his experiments, electrifying the boys there, suspending them, holding the electrified tube to their feet and finding that a brass leaf is attracted to their faces. Gray also showed that electric charges resided on the outside surfaces of bodies as he obtained no attractions inside hollow tubes.

Charles Dufay (1698-1739) in 1733 learned of Gray's experiments, repeated them, and was able almost immediately to state that the difference between electrics and non-electrics was due to their difference in conducting capacity. He found that even the metals could be electrified if they were supported on glass standards, so that the virtue produced by rubbing could not escape from them.

His great discovery, however, was that electricity is of two kinds. Whilst examining the motion produced by an excited glass rod in a piece of gold leaf he brought up a piece of electrified gum copal and to his astonishment observed that instead of being repelled, as it was from the glass, it was strongly attracted. "I cannot doubt," he writes, "that glass and crystal operate in exactly the opposite way to gum-copal and amber, so that a leaf repelled by the former because of the electricity which the leaf contracted will be drawn by the latter, and this leads me to conclude that there are perhaps *two kinds of different electricities*."

He named the electricity produced on glass *vitreous* and that on amber *resinous*, and further established the fundamental law that bodies similarly electrified repel while bodies dissimilarly electrified attract each other.

Dufay thus put an end to the attempts to find new electrics, by showing that all bodies under suitable conditions can be electrified and that, as he wrote: "Electricity is a quality universally expanded in all the matter we know, and which influences the mechanism of the universe far more than we think."

John Canton (1718-1772) discovered in 1753-1754 the facts of induction. He noticed that an insulated body under the influence of a neighbouring charge acquired two charges, the one nearest the influencing charge being of the opposite kind, and the one farthest away being of the same kind, as the inducing charge, and that they disappeared on the removal of the latter. If, however, the

insulated body were touched prior to the removal of the inducing charge it was left with a charge of the opposite kind.

We have now traced through very many centuries the gradual growth of knowledge of the experimental facts of magnetism and electricity. From being regarded as mysterious and isolated properties resident only in the lodestone and amber, we have seen that in the case of one at least, the property was found to be common to all matter. So far there has been no measurement; the next stage in development is concerned very largely with the quantitative aspects of these phenomena, and the suggestion of theories to accord with the facts.

As a hypothesis it was early assumed that all bodies contain equal quantities of two imponderable electric fluids which in the natural state of bodies neutralise each other's effects. The act of electrifying bodies on this theory consisted in separating these fluids, or in the addition or subtraction of one of them. This agreed with the facts that electricity could be conveyed from one body to another and gave a plausible view of the nature of induction in which the inducing body was supposed to attract the opposite kind of electricity to the nearer end, and repel the electricity similar to itself to the further end of the influenced body. The idea of the neutral state being one in which there was no electrification, early led to the naming of the two kinds of electricity positive and negative. Considerations such as these also led to the conception of a magnetic fluid with a similar duplex character.

A modification of the theory suggested by Benjamin Franklin (1706-1790), however, regarded electrification as the adding or subtracting of a quantity of one electric fluid, so that positive electrification was regarded as the addition of this fluid to ordinary matter and negative as a subtraction of it.

Various attempts to discover the law of attraction between magnetic poles and between electric charges were made shortly after the main experimental phenomena of electricity and magnetism had been recognised. Coulomb (1736-1806), in 1785, succeeded in deducing the law by means of his torsion balance. He had previously been investigating the force of torsion and the electricity of thin metallic

wires, and conceived the idea of using his torsion balance for the investigation of the magnetic and electric forces. The principle of the method consisted in measuring the torsion in a fine wire from which was suspended a horizontal magnet in the one case, and a horizontal bar carrying a small electrically charged sphere in the other. Another small charged sphere or another magnetic pole was then placed in the position at which that on the torsion wire had come to equilibrium. The repulsion which occurred was balanced by the consequent torsion in the wire and the distance of this repulsion was varied by varying and noting the amount of additional torsion which had to be applied to the wire in order to bring back the repelled magnetic pole or electric charge to various other distances. Though of necessity, because magnetic poles are not concentrated at unique points nor are charged spheres infinitely small, the ideal conditions are unattainable in practice, yet by using long steel magnets symmetrically magnetised and arranging that disturbing elements were small compared with the effects he was measuring, Coulomb was able to deduce that the forces varied as the inverse square of the distance between the centres of the poles or charges.

He was, however, anticipated in his deduction of this law for the electrical case by Cavendish (1731-1810), who between 1771 and 1781 showed that an electrified sphere inside two metallic hemispheres fitting over it in the form of a sphere without actually touching it, on being brought into contact with the hemispheres gave up all its charge to them. From this he deduced that the law of force must be the inverse square. Cavendish's method of testing for residual electrification on the inner sphere was not sufficiently sensitive to enable him to verify the law to an accuracy greater than 2 per cent. With strange reticence and apparent contempt for the opinions of the world he did not publish these results, and it was not until 1879 that Maxwell discovered them in Cavendish's manuscripts and repeated the experiment with all the improvements possible at that time, and was able to show that if the law of force varied inversely as the $(2 \pm n\text{th})$ power of the distance, then n was less than $1/21600$.

As a direct result of Coulomb's experiments, taken in

conjunction with the other fundamental facts of experiment and the two fluid theory of the nature of electricity and magnetism, these subjects were brought within the realm of mathematical treatment. Accordingly the close of the eighteenth century was marked by great developments on the mathematical side of these subjects, and we find Laplace (1749-1827), Biot (1774-1862) and Poisson (1781-1840) devoting their energy to the innumerable problems which occurred to them.

But other phenomena were shortly to be discovered. No sooner had the real character and mode of action of the electric and magnetic forces been demonstrated than a new source of electricity was made available. The preceding work was a necessary preliminary for the understanding and elucidation of the following.

The discovery marking the new epoch was that of the voltaic battery by Alessandro Volta (1745-1827). Galvani (1737-1798) in 1790 announced his discovery of the muscular contractions which occurred when a nerve and muscle of a newly-killed frog were touched by dissimilar metals which were themselves in contact. He attributed this to what he called "animal electricity." Volta, however, in 1800, as a result of his investigation of the same phenomena, discovered that the mere putting together of the two different metals was sufficient to produce a separation of electricities, or what we should call a difference of potential, and that if a pile of pairs of different metals, for instance zinc and copper, separated by pieces of cloth moistened with diluted acid were taken, the potential difference existing between contiguous pairs was made cumulative. An improvement on this means of obtaining a potential difference was devised shortly after by Volta in his "couronne des tasses," in which connected strips of copper and zinc formed bridges between cups of dilute acid. This discovery roused a great deal of interest, and a large number of scientific workers began experimenting with the voltaic piles or batteries.

The decomposing effect of the battery was early noticed. Nicholson (1753-1815) in 1800 observed the evolution of hydrogen and oxygen from water, while Davy (1778-1829) in 1807 decomposed potash and soda, which up to that time were considered to be elements, and in 1808

with 2000 cells produced an electric arc between carbon poles.

The electricity derived from voltaic batteries was usually referred to as voltaic electricity in contra-distinction to common electricity which was obtained by friction, or by means of the influence machines which developed it by induction from an initial small charge. It was early recognised that the two kinds of electricity had much in common as it had been shown that both produced heating effects in conductors, that both could develop sparks on discharge, and that the electroscope was affected by contact with the ends of a battery of many plates as if these ends were charged negatively and positively. So that quite early on, the conceptions arose that common electricity was electricity in tension, and that voltaic electricity was electricity in motion.

In addition to the similarity noticeable between the two electricities, it was also noticed that electricity in many respects had similar properties to magnetism. Early in the nineteenth century, therefore, we find many experimentalists trying to discover some connection between the two. It was, however, reserved for Hans Christian Oersted (1777-1851) to make the discovery of the relation which was to play such an important part in the further development of the two subjects. In 1820 he found that a compass needle was deflected in the neighbourhood of a voltaic battery whose circuit was completed, and that the direction of the deflection was such as to indicate that a magnetic field was associated with a voltaic current in much the same way as a series of concentric circles is to their common centre. He announced his discovery in Latin in a pamphlet which he circulated to many scientific societies and reviews. His apparatus consisted of a battery of twenty cells, and he investigated what he called the "conflict of the electricity" in the space surrounding the "uniting wire" which connected the poles of his battery. A translation of his paper appeared in the *Annals of Philosophy* in 1820, and the following quotations from it indicate his own view of the phenomena:—

"Let the straight part of this wire (the uniting wire) be placed horizontally above the magnetic needle, properly suspended, and parallel to it. . . . Things being in this

state the needle will be moved, and the end of it next the negative side of the battery will go westward. . . . The effect of the uniting wire passes to the needle through glass, metals. . . . It is needless to observe that the transmission of effects through these matters has never before been observed in electricity and galvanism. . . .

“The electric conflict acts only on the magnetic particles of matter. All non-magnetic bodies appear penetrable by the electric conflict, while magnetic bodies or rather their magnetic particles, resist the passage of the conflict. Hence they can be moved by the impetus of the contending powers. It is sufficiently evident from the preceding facts that the electric conflict is not confined to the conductor, but dispersed pretty widely in the circumjacent space.

“From the preceding facts we may likewise collect that this conflict performs circles; for without this condition it seems impossible that the one part of the uniting wire, when below the magnetic needle, should drive it towards the east, and when placed above it towards the west, for it is the nature of a circle that the motions in opposite parts should have an opposite direction.”

The publication of these results aroused the greatest interest in the question of the connection between electricity and magnetism. Oersted's experiments were repeated all over Europe, and at once a magnificent harvest of new results appeared.

André Marie Ampère (1775-1836) on the 2nd of October, 1820, only a few months after the publication of Oersted's results, presented to the French Academy of Sciences a paper in which he showed that not only is there a mechanical force between an electric current and a magnet, but that there is a mechanical force between two neighbouring electric circuits. In an ingenious series of experiments coupled with mathematical reasoning of a very high order, he investigated the mutual action of two circuits, and deduced the law according to which the hypothetical element of currents, of which he considered his complete circuits to consist, act on each other.

In these experiments he used a suspended movable coil which consisted of two rectangular loops in series placed alongside each other, so that the current in one was in the opposite direction from that in the other. In this way he

made the coil astatic and so got rid of the disturbing effect of the earth's magnetic field. Instead of considering the actual movement of this suspended system, he reduced his experiments to the observation of its equilibrium under the action of an external circuit.

He then showed (1) that two equal currents in opposite directions had no effect on the suspended coil; (2) that if one of these currents had sinuosities in it but was always near to the other which was straight no effect was produced, so that the effect of an element of current was equal to that of its projected length; (3) that no circuit could cause a current element in another circuit to move in the direction of its own length; and (4) that the action of two circuits on opposite sides of the suspended system was nil if one had n times the dimensions of the other but was n times as far removed.

From these observations Ampère succeeded in deducing the laws of the mechanical action between currents. "The whole theory and experiment," writes Maxwell, "seems as if it had leaped full grown and full armed, from the brain of the Newton of electricity. It is perfect in form, and unassailable in accuracy, and it is summed up in a formula from which all the phenomena may be deduced, and which must always remain the cardinal formula of electrodynamics."

As a result of these experiments he showed that parallel currents flowing in the same direction attracted, and in opposite directions repelled each other, and that a current in a single plane was equivalent in its effect at external points, to a magnetic shell, or magnet of extremely short length, and was thence led to his brilliant and pregnant conception that magnetism was due to molecular electric currents.

Ampère was not concerned with the physical reasons underlying the mechanical effects he had elucidated in so wonderful a manner. His object was mainly to "first observe the facts in order to deduce general laws, and to deduce from these laws independently of any hypothesis on the nature of the forces which produce the phenomena, the mathematical value of the forces, that is to say, the mathematical formula which represents them."

Michael Faraday (1791-1867) on the contrary, throughout

the whole of his work was mainly interested in the physical reasons for the phenomena he investigated. His earliest work on electromagnetism seems to have been done in 1821 as an immediate result of Oersted's discovery. Numerous investigators seem to have realised that it ought to be possible to make a magnetic pole revolve continuously round a wire carrying a current, but it was reserved for Faraday to overcome the experimental difficulties. By placing a magnet in a trough of mercury so that about half an inch of it projected above the mercury, and arranging that a voltaic circuit was completed through a wire hanging from a point above the vertical magnet and dipping down into the mercury, but prevented from becoming vertical itself by having a piece of cork at its lower end, he managed to make the wire revolve continuously round the magnet. In a somewhat similar manner he made a magnet revolve round a vertical wire.

His most important contribution to electrical science was made ten years later, in 1831, when he discovered the phenomena of the induction of currents. Analogy with the induction of magnetism and of static electricity had led him to the opinion that some similar effect might be obtained with voltaic currents. His earlier essays in which he tried to get a current in one circuit by means of a current already in existence in another circuit had given him no results. On reapproaching the question in this later year he noticed that if a closed circuit containing a galvanometer but no battery was in close proximity to a second circuit containing a battery, the galvanometer was momentarily deflected when the second circuit was completed or broken. In the next eleven days he completely worked out the conditions under which the induction of currents occurred. His experiments were described at a meeting of the Royal Society in the same year and are to be found in the first two series of his *Experimental Researches*. Here he writes: "Hence it is evident that currents of voltaic electricity present phenomena somewhat analogous to those produced by electricity in tension. . . . The result is the production of other currents (but which are only momentarily) parallel to or tending to parallelism with the inducing current. . . . It was found in all cases that the induced current, produced by the first action of the inducing current, was in the

contrary direction to the latter, but that the current produced by the cessation of the inducing current was in the same direction."

He then tried the effect of winding his two circuits on a ring of iron, and found that the effect was very much increased. This immediately suggested the use of a magnet by itself, and he found that the approach and withdrawal of the magnet produced induced currents also. He writes: "The similarity of action, almost amounting to identity between common magnets and either electro-magnets or volta-electric currents, is strikingly in accordance with and confirmatory of M. Ampère's theory, and furnishes powerful reasons for believing that the action is the same in both cases."

As a result of these investigations he suggested the correct explanation of an observation due to Arago, that if a magnetic needle be suspended over a rotating disc it tends to follow the movement of the disc. This he recognised as being due to induced currents set up in the disc reacting on the magnet and tending to make it rotate in the same direction. He then took a copper disc and mounted it between the poles of a magnet so that it could be rotated, and connected the axle through a galvanometer to a point on the circumference. On rotating the disc he was able to obtain a continuous supply of electricity. This important application of the newly-discovered phenomena, in which he made the first dynamo electric machine, laid the foundations of modern electrotechnics.

Besides discovering the induction of currents by one circuit in another, Faraday discovered an analogous effect in the case of a single circuit. It had been brought to his notice that while it was not possible to get a shock from a voltaic battery of two plates by means of short wires, it was possible if the leads included in their circuit an electro-magnet. His investigations on this subject are described in the ninth series of his *Experimental Researches*. He found that the same piece of wire which when straight would not give him a shock would do so if it were in the form of a helix. Further investigation revealed the extra current at break. "These experiments," he says, "establishing as they did, by the quantity, intensity, and even direction, a distinction between the primary or generating

current and the extra current, led me to conclude that the latter was identical with the induced current described in the first series of the *Researches*, and this opinion I was soon able to bring to proof, and at the same time obtain not the partial but entire separation of one current from the other."

He also remarks that the first thought which arises in the mind is, that the electricity circulates with something like *momentum* or *inertia* in the wire, but he appears to abandon that idea as the same piece of wire exhibits the effect in varying degrees dependent on its geometrical configuration.

In addition to his discoveries in electromagnetism he also placed the science of electrostatics on a firm basis, and discovered the effect which the medium played in many electrostatic problems. This recognition of the influence of the medium in which, however, he had been anticipated by Cavendish, was extremely important as it was owing to his consideration of the effect of the medium that he was led to his conception of lines of force in electric and magnetic fields. He described his experiments on electrostatics in the eleventh series of his *Experimental Researches*. After stating the opinions of Cavendish, Poisson and others who considered "induction as an action at a distance and in straight lines," he gives his own opinion that "ordinary induction is in all cases an action of contiguous particles consisting in a species of polarity," and states that his aim is to find phenomena which would not be consistent with the theory of action at a distance. In support of this he proved that it is impossible to obtain positive electricity without an equal amount of negative electricity, so that they seem to be intimately related. He then performed experiments in which he showed that the action of a charged body on a small test object from which it was separated by a brass hemisphere was actually greater in certain positions further away from the charged body than at certain positions nearer to it. As he remarked: "Here the induction fairly turned a corner. Nothing, in fact, can better show both the curved lines or courses of the inductive action, disturbed as they are from their rectilinear form by the shape, position, and condition of the metallic hemisphere; and also a *lateral tension*, so to speak, of these lines on one another,"

Faraday's discovery of the specific inductive capacity resulted from his experiments on the distribution of electricity between what were really two identically equal Leyden jars having different dielectrics, when a charge possessed by one was shared with the other. He placed a small insulated brass sphere at the centre of each of two equal larger brass spheres containing air as the dielectric. If the inner sphere of one were charged and then allowed to share its charge with the inner sphere of the other he found that the two outer spheres had received the same charge by induction. If, however, the air in one sphere were replaced by sulphur or another insulator, the induced charges on the outer spheres were not equal, the one containing the sulphur receiving the bigger charge. Thus the sulphur transmitted more induction, or as Faraday said, it had a greater "*specific inductive capacity*."

During the whole course of his researches Faraday was guided by the conception that the phenomena of electricity, magnetism, and the new science of electromagnetism were the results of invisible changes in an intervening medium. He was well aware of the distribution of iron filings in the neighbourhood of a magnet, but while to the mathematicians their arrangement merely indicated the directions of the forces at different points, to Faraday they indicated a condition of the medium surrounding it which was inseparable from the magnet. He similarly regarded an electrified body as the origin of a system of lines of electric force attached to the body so long as it was charged. He noticed that most of the phenomena of the electric and magnetic fields could be deduced from the idea that these lines of force which joined positive charges to negative charges had a tendency to contract, that is were in a state of tension and at the same time exerted a lateral pressure on each other. In most of his writings Faraday gives the impression that he regarded the lines of force as chains of polarised particles though in his considerations of a vacuum in his later researches he regards them as having an existence apart from the material particles, as he suggests that the action may be transmitted by the æther which if it exists should have other uses besides the conveyance of radiation.

He also regarded it as probable that the consideration

of lines of force should have a quantitative aspect as he suggested the idea of unit tubes of force whose concentrations were indicative of the field intensity at various points, while in his later explanation of the induction of currents he showed that the quantity of electricity set in motion depended on the number of lines of force due to the inducing system cut by the circuit in which the induction occurs. "Although their forms," he states, "as they exist between two or more centres of power may vary very greatly, and also the space through which they may be traced, yet the sum of the power contained in any one section of a given portion of the lines is exactly equal to the sum of the power in any other section of the same lines, however altered in form they may be."

Although Faraday had so clearly pointed out the importance of the medium in electro-magnetic phenomena, the majority of scientists continued to favour action at a distance.

In 1834 Lenz (1804-1865) announced the important relation between the direction of the induced current and the mechanical action of electric currents known as Lenz's law. It asserts that the induced current is in such a direction that its electromagnetic action on the inducing system is such as to oppose the relative motion which produces it.

Neumann (1798-1895), in 1845, founded his theory of induced currents on this law. By introducing the conception of the potential of one circuit on the other he succeeded in obtaining the laws of the induced current. While Hermann von Helmholtz (1821-1894) in 1851, and shortly afterwards William Thomson (later Lord Kelvin, 1824-1907) independently, by the application of the principle of the Conservation of Energy which had shortly before been enunciated by Helmholtz, showed that the induction of currents was a necessary consequence of Oersted's discovery.

Though the induction of currents could be dynamically accounted for on both Neumann's and Helmholtz' theories, these theories did not lead to any further development of the subject nor did they indicate the possibility of new phenomena. In consequence they were displaced by the electromagnetic theory developed by James Clerk Maxwell (1831-1879), which in its fundamental conceptions was

based on the ideas of Faraday regarding the medium, and which besides including within its scope all the existing electromagnetic phenomena, predicted others of a very remarkable nature, which were in later years verified with conspicuous success.

What distinguished Maxwell's work from that of Neumann, Helmholtz and others, was his revival and insistence on the idea of Faraday that the medium was the seat of the energy of electric and magnetic fields. While an undergraduate at Cambridge he had busied himself in translating the purely physical notions of Faraday into a form suitable for mathematical treatment. Faraday had recognised that the medium in the electromagnetic field was "polarised," and, as has been mentioned, regarded his lines of force somewhat in the nature of chains of polarised particles. Maxwell slightly altered this conception of the state of the medium by substituting for it his conception of "electric displacement," and it is a basic principle in his theory that an electric intensity produces a motion of electricity or electric displacement in the medium, whether the medium be a conductor, a dielectric or a vacuum. In a dielectric and a vacuum the electricity cannot travel far but suffers a slight displacement in the same direction as the electric intensity. Changes in the amount of the electric displacement constitute a current, so that he really introduced the idea of two kinds of current, the first being that due to the ordinary motion of charges in conductors, and the second, that due to a change in the amount of the electric displacement in dielectrics and vacua.

Ampère's work on the equivalence of currents to magnetic shells had led to the deduction that the work done in taking a unit magnetic pole round a wire carrying a current is equal to 4π times the current, expressed in suitable units, and Faraday had shown that in any circuit the electromotive force due to induction is proportional to the rate of change of the number of magnetic lines of force passing through it. By adding to these principles, the assumption that the current due to the change in electric displacement produced the same effects as do ordinary currents he showed that the propagation of electric and magnetic forces took place in the æther with a constant velocity, and from a knowledge of the observed motions of ponderable bodies

in electromagnetic fields constructed a system of forces due to stresses and changes of stress in the æther which would produce the motion in accordance with the laws of dynamics.

These important results were first announced by him before the Royal Society in 1864, and were published in the *Philosophical Transactions* in 1865 under the title of *A Dynamical Theory of the Electromagnetic Field*. Here he also shows that the constant velocity referred to above can be found from a knowledge of the ratio which the two unit quantities of electricity in the electrostatic and electromagnetic systems of measurement bear to each other. Maxwell suggested methods of determining this ratio and was able to prove that it was identical with the number expressing the velocity of light.

Thus he had shown that the medium he postulated as the vehicle of electromagnetic phenomena propagated them with the same velocity as the luminiferous æther propagated light. Realising that it was unphilosophical to have two æthers filling the same space but "if the properties which must be attributed to the medium in order to account for electro-magnetic phenomena are of the same kind as those which we attribute for the phenomena of light, the evidence for the physical existence of the medium will be considerably strengthened," he formulated his electromagnetic theory of light.

Maxwell investigated mathematically the way in which the electric and magnetic forces would be propagated in free space, and showed that in electromagnetic waves the electric and magnetic vibrations occurred at right angles to each other and to the ray, and that they were capable of being polarised and exhibiting double refraction and that the reflection formulæ and the wave surface in non-isotropic media were the same as those given by Fresnel.

As regards the stresses in the æther, we have seen that these stresses and changes in stress constitute electric and magnetic forces but so far have not distinguished between them. Ampère's work on the magnetic fields associated with currents showed that these fields were produced by the motion of electricity, so that electric forces are identified as stresses and the magnetic forces as changes in stress. If we compare the æther to an elastic medium we are led

to regard electric energy as the potential energy of pressures and strains in the medium and magnetic energy as the kinetic energy due to the momentum of the medium resulting from changes in the stresses and strains.

The publication of Maxwell's treatise stimulated in a marked manner interest in electromagnetic phenomena, particularly on the experimental side, and determinations of the velocity of the light and of the ratio between the electrostatic and electromagnetic units were undertaken to test the theory. It appeared from the theory that the refractive index of transparent solids should be equal to the square root of the specific inductive capacity, but the agreement was only approximate in several cases and widely divergent in most, though Maxwell himself pointed out that the discrepancy was probably due to the refractive index being taken for waves of short wave-length whilst the specific inductive capacity was obtained for waves of infinite wave-length, i.e. for steady charges. The discrepancies, however, when the theory was applied to the case of material bodies were sufficient to prevent any general acceptance of the electromagnetic theory, and it was not until Hertz produced electric waves experimentally in 1887 that Maxwell's theory really received general recognition.

Heinrich Hertz (1857-1894) in 1886 commenced an investigation to establish experimentally the fundamental concept that a change in dielectric displacements in non-conductors produced the same electromagnetic effects as did the currents which are equivalent to them in Maxwell's theory. The problem was proposed by the Berlin Academy of Sciences in 1879 and von Helmholtz influenced Hertz to take it up. It was particularly interesting as Helmholtz had succeeded in deducing Maxwell's equations from the older "action at a distance" point of view, though he had to deny necessarily the possibility of the propagation of electromagnetic effects with a finite velocity.

Kelvin in 1853 had shown by the application of the Principle of the Conservation of Energy to the case of the discharge of the Leyden jar, that in certain cases the discharge was oscillatory in character, and that its period depended on the electrical constants of the circuit. This had been verified by Feddersen (1832-1918) shortly after-

wards. Hertz realised the possibility of the spark discharge as a source of oscillating currents which might be capable of detection, and so in 1886 carried out experiments, using as a radiator an induction coil, the secondary of which was connected to two rods in line with each other and having spheres on their inner ends and metal plates at their outer ends. As a detector, he utilised a circuit of wire with a small gap which could be adjusted to any desired length by means of a micrometer. He found that small sparks passed across the terminals of this resonator when it was at certain positions with reference to the radiator. Hertz then proved that this indicated the presence of stationary waves formed by reflection from the walls of his laboratory. The waves he worked with were about 30 cm. long, and he managed with great ingenuity to show that they were propagated in straight lines, that they exhibited polarisation, suffered reflection and refraction and behaved in every respect as invisible light waves of long wave-length. Thus the fundamental concept and abstruse mathematics of Maxwell's theory received splendid and complete verification, while the one *plenum* for the propagation of the phenomena of heat, light, magnetism and electricity became firmly established.

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CHAPTER VIII

HEAT AND THERMODYNAMICS

THOUGH the manifestations of heat and its usefulness in human life have been apparent for so many centuries, it is only within the last 150 years that anything like clear conceptions of the nature of heat have been obtained. From the beginnings of science two diametrically opposed theories regarding its nature have been entertained, one of which has survived to the present day. Accordingly we have firstly, the material or caloric theory of heat, in which heat is supposed to be a subtle elastic fluid which fills up the spaces between the small particles of bodies, and secondly, the theory that heat is nothing more than the energy of the rapid to and fro motion of the small particles themselves.

The latter theory was always held by the minority, but still it is possible to trace it continuously from the time of the ancient Greeks. Plato (*circa* 427-347 B.C.), for example, writes: "For heat and fire which generate and sustain other things, are themselves begotten by impact and friction; but this is motion." Francis Bacon (1561-1626) in his *Novum Organum* summed up the then known facts relating to heat, and after consideration endeavoured to account for them. "When I say of motion," he writes, "that it is the genus of which heat is a species, I would be understood to mean, not that heat generates motion, or that motion generates heat (though both are true in certain cases), but that heat itself, its essence and quiddity, is motion and nothing else. . . . Heat is a motion of expansion, not uniformly of the whole body together, but in the smaller parts of it, and at the same time checked, repelled, and beaten back, so that the body acquires a motion alternative, perpetually quivering, striving, and

struggling, and irritated by repercussion, whence springs the fury of fire and heat." Robert Boyle (1627-1691), too, appears to have had a remarkably clear idea of the generation of heat by the "nimble hammering of iron by three lusty men." The following passage is really remarkable: "If a somewhat large nail be driven by a hammer into a plank, it will receive divers strokes on the head before it grows hot; but when it is driven to the head, so that it can go no farther, a few strokes will suffice to give it a considerable heat; for whilst at every blow of the hammer, the nail enters farther and farther into the wood, the motion that is produced is chiefly progressive, and is of the whole nail tending one way; whereas, when that motion is stopped then the impulse given by the stroke, being unable either to drive the nail further on, or destroy its entireness, must be spent in making a various, vehement, and intestine commotion of the parts themselves, and in such an one we formerly observed the nature of heat to consist."

Robert Hooke (1635-1703) also attributed heat to the motion of the small particles of bodies. In his *Micrographia* (1664) in discussing "fluidness," he writes: "First what is the cause of fluidness? And this I conceive to be nothing else but a certain pulse or shake of heat; for heat being nothing else but a very brisk and vehement agitation of the parts of a body (as I have elsewhere made probable) the parts of a body are thereby made to loose from one another that they may easily move any way and become fluid," and later: "Now that the parts of all bodies though never so solid do yet vibrate, I think we need go no further for proof than that all bodies have some degree of heat in them, and that there has not yet been found anything perfectly cold. Nor can I believe indeed that there is any such thing in nature as a body whose particles are at rest or lazy and inactive in the great Theatre of the World, it being quite contrary to the grand Economy of the Universe."

In spite of the favour which some of the greatest intellects showed to the vibratory theory of the nature of heat, the majority of men accepted the material view. This was particularly so after Newton's time as his great work in dynamics and optics seems to have prevented due attention being given to vibratory theories, though he himself

inclined to such a theory of heat radiation. The material theory is most intimately connected with the phlogiston theory outlined in Chapter III, phlogiston being identified with heat or caloric.

The name "caloric" was first used by Lavoisier (1743-1794) in 1789, who as we have seen overthrew the phlogiston theory. He seems to have believed that heat was a "fluid eminently elastic," though later on in the same work he writes that it is not necessary to assume that caloric is a real substance, it being sufficient from the mathematical point of view to regard it as "some kind of repulsive effect which keeps the molecules apart."

The caloric theory postulated the existence of an all-pervading, highly elastic fluid, the particles of which were attracted by matter but repelled each other. On this view, if bodies at different temperatures were placed in contact, caloric would pass from the hotter to the colder until a statical equilibrium under the resultant systems of attraction and repulsion was obtained. Thus the fact that bodies expanded when caloric was transferred to them was accounted for by the self-repellent property of the fluid. The heat fluid was also considered to be imponderable, indestructible and uncreatable. All heat phenomena were therefore regarded as due to the movement of caloric from one place to another. This conception explained many of the facts by which it could be tested—granted the assumption—the deductions were quite logical and apparently satisfactory.

However, as more and more phenomena became known, the original postulates of the theory hardly proved adequate to the task of accounting for them, so additional attributes of either caloric or matter were assumed in order to make the facts fit in with the theory. Thus in explaining the development of heat by friction and by the compression of gases, it was assumed that the act of friction abraded portions of a body and that the capacity for heat of the abraded particles was less than that of the substance to which they belonged, so that caloric was liberated; or that friction and pressure squeezed out latent caloric which then became apparent or sensible caloric.

The theory rose to its highest position as an intellectual philosophy under the labours of Joseph Black (1728-1799),

whose work in connection with phlogiston we have considered in a previous chapter, and it was probably on account of his work on caloric that he remained a phlogistonist all his life in spite of his discovery of facts so much at variance with the phlogiston theory.

Up to his time it was believed that the quantities of heat necessary to change the temperatures of different bodies by the same amounts were proportional to the weights of the bodies, or in other words the thermal capacities of equal weights of all bodies were the same. In his *Lectures on the Elements of Chemistry*, he writes: "But very soon (1760) after I began to think on this subject, I perceived that this opinion was a mistake, and that the quantities of heat which different kinds of matter must receive, to reduce them to equilibrium with one another, or to raise their temperatures by an equal number of degrees, are not in proportion to the quantity of matter in each, but in proportions widely different from this. . . . This opinion was first suggested to me by Dr. Boerhaave (*Elements of Chemistry*). After relating the experiment which Fahrenheit made at his desire, by mixing hot and cold water, he also tells us that Fahrenheit agitated together quicksilver and water unequally heated. From the doctor's account it is quite plain that quicksilver, though it has thirteen times the density of water, produced less effect in heating or cooling water to which it was applied than an equal measure of water would have produced. He says expressly that the quicksilver never produced more effect in heating or cooling an equal measure of water than would have been produced by water equally hot or cold with the quicksilver and only two-thirds of its bulk." Black was thus led to the idea of the specific heats of substances or the ratios of their thermal capacities to that of an equal quantity by weight of water.

He also investigated the changes of temperature which occurred whilst a body passed from the solid to the liquid state. It was believed, until he showed the contrary, that when a solid was changed into a liquid or a liquid into a gas by the application of heat, the whole of the heat supplied manifested itself as a rise in temperature. Black showed that a body could receive heat but not indicate any rise in temperature. In these cases he assumed that the heat was really present but latent, and that latent heat did not

affect a thermometer as did sensible heat. He realised that this heat was recoverable in the converse processes of condensation and freezing. "The opinion I formed from attentive observation of the facts and phenomena," he writes, "is as follows: When ice, for example, or any other solid substance, is changing into a fluid by heat, I am of opinion that it receives a much greater quantity of heat than what is perceptible in it immediately after by the thermometer. A great quantity of heat enters into it on this occasion without making it apparently warmer when tried by this instrument. This heat, however, must be thrown into it, in order to give it the form of a fluid; and I affirm that this great addition of heat is the principal and most immediate cause of the fluidity induced."

The first to investigate the problems of heat without prejudice in favour of any particular theory was Count Rumford (1753-1814). While in the service of the Elector of Bavaria he was much struck with the amount of heat which was produced in the boring of cannon. As we have mentioned above the calorists explained this by assuming that the metallic chips detached from the cannon during the boring process had less capacity for heat than the metal, owing to their latent caloric being squeezed out of them and its consequent liberation as sensible heat. Rumford was impressed with the apparently inexhaustible source of heat, so he commenced a series of experiments having for their object the elucidation of the origin of this heat. His first experiments took the form of showing that the hypothetical caloric had no weight. These were followed by the experiments described in the *Philosophical Transactions* of the Royal Society for 1798 in a paper entitled *An Experimental Enquiry concerning the Source of the Heat which is Excited by Friction*. In these experiments he caused the short cylinder of brass, which was usually cast with a cannon and attached to it by a short neck, to be made hollow, and arranged a mechanism by which "a blunt borer could be forced against its solid bottom at the same time that it should be turned round its axis by the force of horses." The borer was pressed against the bottom by means of a screw with a force which he calculated to be equal to the weight of 10,000 lbs. With this apparatus and with the cylinder turning 32 times per

minute he found that in thirty minutes the mean temperature of the cylinder was raised from 60° F. to 130° F., whilst 837 grains troy of metal were reduced to metallic dust. As a result of experiment he then found that the capacity for heat of the metallic dust was the same as the metal from which they came, and so concluded that "the Heat generated in these experiments, or *excited*, as I would rather choose to express it, was not furnished *at the expense of the latent Heat or combined caloric* of the metal."

In a further experiment he surrounded the brass cylinder with a wooden trough of water and repeated the same procedure and writes: "At the end of 1 hour I found, by plunging a thermometer into the water in the box, . . . that its temperature had been raised no less than 47° , . . . At the end of 2 hours reckoning from the beginning of the experiment, the temperature of the water was found to be raised to 178° . At 2 hours 20 minutes it was at 200° ; and at 2 hours 30 minutes it actually boiled! . . . By meditating on the result of all these experiments we are naturally brought to that great question which has often been the subject of speculation among philosophers; namely, what is heat? Is there any such thing as an igneous fluid? Is there anything that can with propriety be called caloric?" After considering the possible sources that might be suggested as the origin of the heat and proving that these are impossible, he summed up the matter in these words: "It is hardly necessary to add, that anything which any *insulated* body, or system of bodies, can continue to furnish *without limitation*, cannot possibly be a *material substance*; and it appears to me to be extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in the manner the Heat was excited and communicated in these experiments, except it be motion."

Still the calorists were not convinced; it seems that the term "capacity for heat" had not received a unique connotation, as, in addition to meaning the amount of heat required to raise the temperature of unit mass of a substance through 1° , it was also used in a way which indicated that it meant the total heat content of a body. Rumford had not shown that the total heat content of the metallic chippings was the same per unit mass as that of the brass

of the cannon, so that the calorists were logically correct in their insistence on this point though it would have been pardonable had they discarded their logic and considered the fact that heat could be produced without limitation, which Rumford seems to have regarded as the determining factor.

Had Rumford shown that the metallic chips required the same quantity of heat to melt them as did an equal quantity of the brass, and had it been conceded that the homogeneous brass thus obtained had the same total heat content per unit mass as had the brass of a cannon, Rumford's deduction would have been completely established. This was not done, however, and it was left for Sir Humphrey Davy (1778-1829) in 1799 to make the crucial experiment. It was a fact of observation, admitted by the calorists, that the capacity for heat, in the sense of total heat content, of a mass of water was greater than that of an equal mass of ice, as the ice in melting was known to absorb a large quantity of heat which did not affect the thermometer. Davy rubbed two pieces of ice together and showed that as a result they melted. The heat required to do this could not conceivably be regarded as having its origin in anything except the motion which produced it.

In marked similarity to the phlogiston theory the caloric theory manifested great vitality, and in thinking of the reasons for this it must be granted that it certainly satisfied many distinguished scientists, for throughout a great many changes it was recognised that a quantity of heat was constant—that what was taken from one place reappeared in another, and that it was subject to the laws of algebra, as the number representing it could be used in calorimetric equations with marked success. On the other hand, the conception of a quantity of motion was not very easily visualised, nor was this possible until the conception of energy (another imponderable) had arisen, and its measurement in terms of *vis viva* or of the work done, or capable of being done, in changing motion had been extended from mechanics to the other branches of natural philosophy.

The development of our knowledge concerning heat is very intimately connected with the investigation of the properties of gases, so that it will be opportune at this

point to consider the work of a number of investigators on the problems presented by gases.

One of the most characteristic properties of a gas is the readiness with which it alters in volume under the action of change of pressure or change of temperature. Robert Boyle (1627-1691) was the first to investigate the changes in volume which occurred in a given mass of air maintained at constant temperature when the pressure to which it was subjected was varied. His results were published in 1662 in his *Defence of the Doctrine touching the Spring and Weight of the Air*, and the following extract from this work gives an interesting account of his experiments. After describing the construction and use of a U-tube, one limb of which was closed, containing a quantity of mercury in the curved portion, he writes: "We began to pour Quicksilver into the longe leg of the siphon, which by its weight pressing up that in the shorter leg, did by degrees streighten the included air, and continued this pouring in of Quicksilver till the Air in the shorter leg was by condensation reduced to take up but half the space it possess'd (I say, *possess'd* not *fill'd*) before; . . . we observed that the quicksilver in that longer part of the tube was 29 Inches higher than the other. Now that this observation does both very well agree with and confirm our *Hypothesis* will be easily discerned by him that takes notice that we teach . . . that the greater the weight is that leans upon the Air, the more forcible is its endeavour of Dilatation, and consequently its power of resistance (as other Springs are stronger when bent by greater weights)." He then calculated "what the pressure should be according to the *Hypothesis* that supposes the pressures and expansions to be in reciprocal proportion," and found very good agreement between the calculated and observed values, for values of the pressure varying from four atmospheres to one thirty-second of an atmosphere. The statement of result of these experiments is usually referred to as Boyle's Law, and is represented by the equation $p v = C$ where C is a constant for a given mass of gas at any given temperature, and p and v are corresponding values of its pressure and volume.

The law of expansion under constant pressure with change of temperature in the case of air was investigated by John

Dalton (1766-1844) and Gay-Lussac (1778-1850) in 1802. Their experiments indicated that the volume of air under constant pressure increased by $1/267$ of its volume at 0°C . for each 1°C . rise in temperature. The French physicist Charles (1746-1823) seems to have discovered that the coefficient of expansion was practically the same for all the commoner gases, while Regnault (1810-1878) showed that the coefficient should be $1/273$. As a deduction from the results of these experiments it followed that the volume of a gas should be proportional to its temperature reckoned from an artificial zero of temperature 273°C . below the freezing-point of water, so that if T denote the temperature measured on the new scale the law of expansion may be combined with Boyle's Law in the form $p v = RT$. If equal volumes of different gases are taken at the same temperature and pressure then R is the same for all, whilst if equal masses are taken the constant R varies inversely as the molecular weight.

Dalton also tried to measure the increase in temperature which occurred when a gas was suddenly compressed. Laplace (1749-1827) saw in this phenomenon a possible explanation of the difference in the velocity of sound as actually observed and as calculated by Newton from considerations based on Boyle's Law. He perceived that the increase in pressure due to a sudden compression would be greater if no heat were allowed to escape, i.e. if the compression were adiabatic, than if it were isothermal. He then showed that to reconcile Newton's results with experiment the ratio of the adiabatic elasticity to the isothermal elasticity should be 1.41 , and that this must also be the ratio of the specific heats determined under conditions of constant pressure and constant volume. The ratio of the two elasticities was determined in 1819 by Clément (d. 1841) and Desormes (1777-1862) to be 1.354 . Dulong (1785-1838) shortly afterwards, through observations on the changes in temperature of different gases under the same compression, which were shown to be inversely as their specific heats at constant volume, deduced that equal volumes of all gases under the same conditions of temperature evolved equal quantities of heat on being submitted to the same compressions. From this it may be further deduced that the difference between the two specific heats

represents the heat absorbed by unit mass of a gas when it increases in volume at constant temperature by $1/273$ of its volume at 0°C . This result, however, had been obtained shortly before on theoretical grounds by Carnot.

We have seen how the experiments of Rumford and Davy on the generation of heat by mechanical means led to the foundation of a mechanical theory of heat. The converse problem of the production of mechanical effects by means of thermal agencies was not dealt with by them. The development of the steam engine by James Watt (1736-1819) and others, about 1780, in which mechanical effect is obtained from a thermal origin, focused attention on this problem in the early years of the nineteenth century, and as a result of experiment and theory in two directions there arose the conceptions which ultimately led to the establishment of the two laws of thermodynamics. In one of these the principal object of consideration was the nature of the relationship between heat and mechanical force, while in the other the subject of enquiry was the efficiency of the sources of obtaining mechanical effect from heat in engines, either actual or imaginary. We now propose to deal with the development of the former line of enquiry.

Séguin (1786-1875) in his *De l'influence des chemins de fer*, published in 1839, considered the production of motive power from heat in the expansion of steam and its consequent cooling, and remarked that it was absurd to suppose "a finite quantity of heat could produce an indefinite quantity of mechanical action, and that it was more natural to suppose that a certain quantity of heat disappeared in the very act of producing motive power." Séguin made experiments to prove this statement, but the results were not decisive, and it was not until 1862 that Hirn (1815-1890) showed by direct experiment that the heat given to the condenser in a steam engine was less than that taken from the boiler, after all corrections possible had been made. Séguin assumed that the loss of heat in the steam was equivalent to the mechanical effect produced by the expansion, and made a rough calculation of the mechanical equivalent of heat.

J. R. Mayer (1814-1878) in 1842, in a paper entitled *Bemerkungen über die Kräfte der unbelebten Natur*, definitely

stated the equivalence of heat and work. He assumed that the heat evolved by compression of a gas was the equivalent of the work done in the compression. From this he deduced that the mechanical equivalent of the heat required to raise the temperature of 1 kilogram of water 1°C . was 365 kilogrammetres. The assumption he made had no experimental basis at the time; all that the results of Dulong had shown was that the heat evolved in the compression of a gas was proportional to the compression, that is, to the work done. In extending the notion of proportionality to that of equivalence Mayer implied that the mere expansion or compression of a gas did not involve the performance of work against the attractive forces between the molecules. In a later paper on *Organic Motion* published in 1845, he referred, in support of this assumption to the experiment of Gay-Lussac in 1807, which showed that when a gas in a closed vessel was allowed to expand into another equal vessel which was evacuated, the rise in temperature of the latter was equal to the fall in temperature of the former, so that the mere expansion of a gas involved no performance of work. In this paper he also enunciated the law of the conservation of force (or energy as we should now say), and after considering the relationships and transformations of the principal forms of energy as manifested in inorganic and organic matter he laid it down as an axiomatic truth that "just as in the case of matter, so also in the case of force, only a transformation but never a creation takes place."

Mayer was really led to his anticipations of these important facts by his fearless application of the dogmas "*causa æquat effectum*" and "*ex nihilo nil fit*." Though his conclusions did not receive experimental verification for some time there is no doubt that he made an important contribution to science.

The experimental evidence of the truths expressed by Mayer were supplied by James Prescott Joule (1818-1889), who in 1839 commenced a long series of experiments in which he investigated the relationship between electrical energy, chemical energy and heat which he showed were mutually equivalent. It is quite probable that even at this date he could have made the same conclusions regarding the conservation of energy that Mayer made, but as he himself

states: "My course, on the contrary, was to publish only such theories as I had established by experiments calculated to commend them to the scientific public being well convinced . . . that hasty generalisation is the bane of science."

In these experiments he showed that the heating effect of a galvanic battery in a wire was proportional to the square of the current and to the resistance, and established what is now known as Joule's Law. He then correlated the heating effect to the chemical action in the battery by showing that it was proportional to the number of chemical equivalents electrolysed, and to the heat of recombination of the chemical equivalents of the products of electrolysis in the battery. By passing the same current through a wire and also a water voltameter he demonstrated that the heating effect was less in the latter than the former, and that the deficiency was just made up by allowing the hydrogen to burn in the oxygen.

These experiments thus showed that definite relationships existed between heat and chemical change. In January, 1843, he extended his experiments to include consideration of mechanical effect, and was able to show that a certain mechanical effect could produce the same amount of heat either directly through friction or indirectly by working a magneto-electric machine and allowing the electric current to heat a conductor. Thus he writes: "However we arrange the voltaic apparatus, and whatever cells of electrolysis we include in the circuit, the whole caloric of the circuit is accounted for by the whole of the chemical change." Later in 1843, anticipating the results of experiments which he shortly afterwards performed, he states: "I have little doubt that by interposing an electromagnetic engine (i.e. motor) in the circuit of a battery, a diminution of the heat evolved per equivalent of chemical change would be the consequence, and in proportion to the mechanical power obtained." In a later paper in the same year entitled *On the Calorific Effects of Magneto-Electricity and on the Mechanical Value of Heat*, he proves that there is a production of heat at every point of the circuit carrying a current, that no part of the whole magneto-electric machine (i.e. dynamo) suffers a fall in temperature, so that the heat production is not due to a transference of heat from one part of the system to another.

As a result of these experiments he was able to write: "We have, therefore, in Magneto-electricity an agent capable, by simple mechanical means, of destroying or generating heat." By a very ingenious arrangement he succeeded in measuring the heat produced and the work done in turning the magneto-electric machine, and found that 838 foot-pounds of work was the mechanical equivalent of the amount of heat required to raise the temperature of one pound of water by 1° F. Joule announced his result to the British Association Meeting at Cork in August of that year, but his conclusion of the mutual "convertibility of heat and mechanical power, according to the above numerical relations," was received in silence and incredulity.

Undaunted, however, by the reception of these experiments he continued his work of finding the mechanical equivalent in a number of different ways. By forcing water through small holes he measured the heating produced by friction and also the work done in forcing it through the holes, and found the equivalent of 770 as compared with 838. In a paper published in 1845 on the *Changes in Temperature produced by the Rarefaction and Condensation of the Air*, he described experiments in which he measured the quantities of heat concerned and the mechanical effect required to produce them, and deduced the value 798 as the equivalent. He also in this paper described his repetition of Gay-Lussac's experiment of 1807 which had been taken by Mayer as justifying the assumption that no internal work was involved in the mere expansion or compression of a gas. His experiments showed that there was no absorption of heat when a gas was allowed to expand and do no external work, that is no internal work was done in expanding, and hence Mayer's assumption was correct.

Joule continually improved his methods of determining the mechanical equivalent which is usually denoted by J. His later method utilised the heat developed by friction when a paddle-wheel rotated in a liquid. As a mean of his best experiments Joule considered 772 foot-pounds to be the most probable value of J.

The experiments of Joule unquestionably demonstrated that the same amount of work, however expended, always developed the same amount of heat, that is, heat and work are equivalent and interchangeable. As a result of these

ideas there now arose the conception of energy or the power of producing work. Heat has the power of producing work so that it is a form of energy, and Joule's experiments showed that the total energy involved in them was constant, that it merely suffered transformation—what was lost as work being gained as heat. In this case we have absolute proof of the conservation of energy. As applied to the relationship of heat and work this generalisation is usually called the First Law of Thermodynamics.

At the same time as Joule was performing his celebrated experiments, von Helmholtz (1821-1894) was studying the problem from the theoretical point of view, and in a memoir published in 1847 entitled *Über die Erhaltung der Kraft*, he definitely stated the principle as applying throughout the whole range of natural phenomena. He traced the transformations of energy in many cases, and showed that the sum total for an isolated system was constant. In the above-mentioned paper he states: "In all cases of the motion of free material points under the influence of their attractive and repulsive forces whose intensities depend solely upon distance, the loss in tension is always equal to the gain in *vis viva*, and the gain in the former equal to the loss in the latter. Hence *the sum of the existing tensions and vires vivæ is always constant*. In this most general form we can distinguish our law as *the principle of the conservation of force*."

Helmholtz then submitted the results of the application of the principle to various physical problems "to a comparison with what experience has established in various branches of physics." Dealing first with simple mechanical problems, including the motions of perfectly elastic solid bodies where the principle was first recognised, he then investigated "the mechanical processes in which an absolute loss of force has hitherto been considered," such as in the collision of inelastic bodies and in the operation of friction. He finally considered a number of electrical phenomena.

Summarising the results of his masterly investigation he declares: "By what I have laid down in the foregoing pages, I believe I have proved that the law in question does not contradict any known fact in natural science, but in a great number of cases is, on the contrary, corroborated in a striking manner. I have endeavoured to state in the most complete manner possible the inferences which flow

from a combination of the law with other known laws of natural phenomena, and which still await their experimental proof. The object of this investigation was to lay before physicists as fully as possible the theoretical and practical importance of a law whose complete corroboration must be regarded as some of the principal problems of the natural philosophy of the future."

Helmholtz was anticipated in his statement of the principle by Colding (1815-1888), who in a thesis on Energy written in 1843, states that "Energy is unperishable and immortal, and therefore wherever and whenever energy seems to vanish in performing certain mechanical, or other work, it merely undergoes a transformation, and reappears in a new form, but the total quantity of energy still abides." Colding's work, however, was tinged with metaphysical considerations, and does not appear to have been known by his contemporaries.

The conception of the conservation of energy, like that of the conservation of mass, has been extremely useful in assisting in the elucidation of many phenomena. In Helmholtz' case he deduced the principle from Newtonian mechanics and the assumption that perpetual motion is impossible, and the agreement of the mode of action of all known forms of energy with this principle has led to its application as one of the tests of all mechanical theories of phenomena inasmuch as they must not violate the principle.

The converse problem of the production of mechanical effect from thermal agencies was first investigated by Sadi Carnot (1796-1832), a young French engineer. In 1824 he published his conclusions in a paper entitled *Reflexions sur la puissance motrice du feu*. Carnot believed in a material theory of heat, but his method of considering the problem, and many of the results he obtained, are independent of any particular theory of heat.

He first of all obtained a clear idea of the essential features of the mechanism by which mechanical effect could be produced from heat. These he showed to be the existence of a difference of temperature by means of which heat is abstracted from a body at the higher temperature and given to one at the lower, and a working substance which by means of its changes in temperature and volume

transfers heat from one body—the source, to another—the refrigerator, at a lower temperature and at the same time gives mechanical effect. He supposed that the motive power arose from the mere transfer of heat, or as he writes : “ the production of the motive power in the steam engine is therefore not due to a real consumption of caloric, but due to its transfer from a hotter to a colder body.” In order to obtain quantitative results from consideration of these changes he made use of a fundamental axiom which he stated as follows : “ In our demonstrations we tacitly assume that after a body has experienced a certain number of transformations, if it be brought identically to its primitive state as to density, temperature, and molecular constitution, it must contain the same quantity of heat as that which it originally possessed ; or, in other words, we suppose that the quantities of heat lost by the body under one set of operations are precisely compensated by those which are absorbed in the others. This fact has never been doubted ; it has at first been admitted without reflection, and afterwards verified in many cases, by calorimetical experiments. To deny it would overturn the whole theory of heat, in which it is the fundamental principle. It must be admitted, however, that the chief foundations on which the theory of heat rests would require a most attentive examination. Several experimental facts appear nearly inexplicable in the actual state of this theory.”

The next essential was to have a perfect engine, that is, the engine which would produce from a given quantity of heat the maximum amount of work possible. Obviously in such an engine there must be no direct transference of heat between bodies at sensibly different temperatures, as it was a matter of observation that the *direct* transference of heat between two such bodies was unaccompanied by mechanical effect. Thus, in the most efficient engine and the cycle of operations which bring it back to its original physical state, the working substance must always be in equilibrium both with its surroundings and with itself, and in addition there must be no friction.

Carnot then described a cycle of operations in which these conditions were satisfied. The first cycle was considered with reference to a mixture of water and steam in a cylinder, the second to a quantity of gas. The following

is a brief summary of his description of the cycle in the second case :—

“ Let us imagine an elastic fluid, atmospheric air, for example, enclosed in a cylinder fitted with a moveable piston. Let there also be two bodies A and B, each maintained at a constant temperature, that of A being more elevated than that of B. Let us suppose the following series of operations to be performed :—

- “(1) Contact of the body A with the bottom of the cylinder which we will suppose to transmit heat easily. The air is now at the temperature of the body A.
- “(2) The piston is gradually raised. The body A furnished the heat necessary to maintain the constancy of temperature.
- “(3) The body A is removed, and the air expands without receiving heat and its temperature falls. Let us imagine that it falls until it is just equal to that of the body B.
- “(4) The air is placed in contact with the body B ; it is compressed by the return of the piston to its original position. The air remains meanwhile at constant temperature, because of its contact with the body B to which it gives up its heat.
- “(5) The body B is removed, and the compression of the air continued. The air being isolated rises in temperature. The compression is continued until the air has the temperature of the body A.
- “(6) The air is placed in contact with the body A and the piston rises to the position it had at the end of the second operation, the temperature remaining constant.
- “(7) The period described under (3) is repeated, then successively the periods (4), (5), (6) ; (3), (4), (5), (6), and so on.

“ During these operations the air enclosed in the cylinder exerts an effort more or less great on the piston. The pressure of the air varies both on account of changes of volume and on account of changes of temperature ; but it should be observed that for equal volumes, that is to say for like positions of the piston, the temperature is higher during the dilatation than during the compression. Since

the pressure is greater during the expansion, the quantity of motive power produced by the dilatation is greater than that consumed by the compression. We shall thus obtain a balance of motive power which may be employed for any purpose. The air has served as working substance in a heat engine ; it has also been employed in the most advantageous manner possible, since no useless re-establishment of the equilibrium of heat has been allowed to occur."

Since infinitesimally small changes of pressure and temperature are sufficient to upset equilibrium and so reverse the direction of the motion and the transfer of heat, such a cycle is reversible, and whatever mechanical effect is derived from the transference of heat in the first case an equal amount spent in working backwards will produce an equal reverse thermal effect. That such a cycle is the most efficient, and that in addition is independent of the nature of the working substance, Carnot showed by assuming a second reversible engine more efficient which could operate between the same two temperatures and drive the first one backwards, thus restoring the source and refrigerator to their original physical condition and leaving a balance of work, which supposition could not be entertained. From these results he concluded that " the motive power obtainable from heat is independent of the agents employed to realise it. The efficiency is fixed solely by the temperature of the bodies between which, in the last resort, the transfer of heat is effected."

Carnot compared the production of work from heat with that from the fall of water in a water-wheel. Thus he states : " According to the views now established we may with propriety compare the motive power of heat with that of a water fall ; both have a maximum which cannot be surpassed, whatever may be, on the one hand, the machine used to receive the action of the water and whatever, on the other hand, the substance used to receive the action of the heat. The motive power of falling water depends on the quantity of water and on the height of its fall ; the motive power of heat depends also on the quantity of caloric employed and on what might be called, which we in fact will call, *its descent*—that is to say, the difference in temperature of the two bodies between which the exchange of caloric is effected. In the fall of water the motive power is strictly

proportional to the difference of level between the higher and lower reservoirs. In the fall of caloric the motive power doubtless increases with the difference of temperature between the hotter and colder bodies, but we do not know whether it is proportional to that difference."

Carnot also showed by calculation based on the known physical constants of water, alcohol and air, that the efficiency was independent of the working substance, but he was unable to determine the form of the function which gave the ratio between the work done and the quantity of heat transferred from the source to the refrigerator. He did, however, deduce that for the same difference of temperature it was greater the lower the temperature of the source.

Only a few copies of Carnot's essay were published, so that its importance was not realised for some time. Clapeyron (1799-1864) in 1832 published an analytical account of Carnot's work in which he made use of the indicator diagram. In this paper, however, he made the fatal mistake of defining the cycle of operations in such a manner that the heat given to the refrigerator is equal to that taken from the source, which though implied by Carnot in his axiom did not form an explicit part of the cycle of operations in his reversible engine, the theory of which is independent of whether these quantities of heat are equal or not. Clapeyron also brought forward experimental data and calculated the amounts of mechanical effect due to a unit of heat descending a degree of the air thermometer in different parts of the scale.

It was through this paper by Clapeyron that William Thomson (afterwards Lord Kelvin, 1824-1907) became acquainted with Carnot's work. He immediately recognised the possibility of constructing an absolute scale of temperature, absolute inasmuch as it would be independent of the properties of any thermometric substance, and in a paper published in 1848 he suggested that equal degrees of temperature should be such that a unit of heat in descending through them should produce equal amounts of work. Thomson calculated from much better data of Regnault (1810-1878) on the properties of steam, the amounts of work produced by a unit quantity of heat in descending a degree of temperature at different parts of the gas scale. These amounts he showed to vary, being higher

at lower parts of the scale than at higher, so that the proposed scale of temperature would differ considerably from the gas scale. He modified the method of graduation on this new scale after he had realised the error in Carnot's axiom, but we shall return to this later.

Thomson spent several years (1847-1851) studying the problem presented by Carnot, and the results of Joule's experiments. In 1848 in the paper just considered, we find him stating that "the conversion of heat or caloric into mechanical effect is probably impossible, certainly undiscovered," though in a footnote he mentions that Joule maintained the contrary opinion as a result of experiments on the friction of fluids in motion, and the calorific effects of magneto-electric machines. He met Joule later in that year, and made him acquainted with Carnot's work. Joule, however, would not accept the second part of Carnot's fundamental axiom, as his experiments in the rarefaction and compression of the air, and also on the heat developed by voltaic batteries with and without electromagnetic engines in circuit, had led him to the conclusion that in the production of work from a thermal agency a quantity of heat proportional to the work done was put out of existence. To quote his own words from his paper on the rarefaction and condensation of the air: "The principles I have adopted lead to a theory of the steam engine very different from the one generally received, but at the same time much more concordant with facts. It is the opinion of many philosophers that the mechanical power of the steam engine arises simply from the passage of heat from a hot to a cold body, no heat being necessarily lost during the transfer . . . Mr. E. Clapeyron agrees with Mr. Carnot in referring the power to *vis viva* developed by the caloric contained in the vapour in its passage from the temperature of the boiler to that of the condenser. I conceive that this theory, however ingenious, is opposed to the recognised principles of philosophy, because it leads to the conclusion that *vis viva* may be destroyed by an improper disposition of the apparatus: thus Mr. Clapeyron draws the inference that 'the temperature of the fire being 1000° (C.) to 2000° (C.) higher than that of the boiler, there is an enormous loss of *vis viva* in the passage of the heat from the furnace into the boiler.' Believing that the

power to destroy belongs to the Creator alone, I entirely coincide with Roget and Faraday in the opinion that any theory, which when carried out, demands the annihilation of force, is necessarily erroneous. The principles, however, which I have advanced in this paper are free from this difficulty. From them we may infer that the steam, while expanding in the cylinder, loses heat in proportion to the mechanical force which it communicates by means of the piston, and that on the condensation of the steam the heat thus converted into power is *not* given back. Supposing no loss of heat by radiation, etc., the theory here advanced demands that the heat given out in the condenser shall be less than that communicated to the boiler from the furnace, in exact proportion to the equivalent of the mechanical power developed."

Thus in 1844 Joule was in possession of the true theory of the steam engine. Thomson, however, though he appreciated the inconsistency between the second part of Carnot's axiom and Joules' results, did not see his way to discard the former for some considerable time. In 1848 he gave *An Account of Carnot's Theory on the Motive Power of Heat*, and in a footnote refers to this difficulty, but he still preferred to follow Carnot. In the same footnote he also raised the question as to what became of the mechanical effect which might be produced if the "thermal agency" be spent in conducting heat through a solid, urging that "nothing can be lost in the operations of nature—no energy can be destroyed." In consequence of his apparent unwillingness to consider the problems on the basis of the new theory of Joule he was anticipated in the production of a true dynamical theory of heat.

The first statement of the true theory based on the idea that the work done in a Carnot cycle is to be accounted for by the excess of the heat received from the source over that given to the refrigerator is due to R. J. Clausius (1822-1888), in a paper entitled *On the Motive Power of Heat and the Laws which can be deduced from it for the Theory of Heat*, read to the Berlin Academy of Sciences in 1850. In the first part of this paper he dealt with the mechanical effects of heat in perfect gases, using the idea of the equivalence of heat and work, which equivalence he explicitly states. He distinguished between the external work done

by a gas in expanding against external pressure, and the internal work done by the particles of the gas in increasing their relative distances, and states it to be highly probable that in perfect gases the internal work is inappreciably small, seeming to show that he was unacquainted with Joule's work on this matter.

In the second part of the paper he corrected Clapeyron's account of Carnot's cycle, bringing it into harmony with the relation between heat and work, showing that the heat which disappears and does work is a function solely of the temperature at which the change takes place, and deducing that the value of "*Carnot's Function*" is the reciprocal of the absolute temperature on the perfect gas scale. The great point in this work is his proof that Carnot's principle of reversibility and consequent maximum efficiency is still true, in spite of the heat taken from the source being greater than that given to the refrigerator. In the proof of this he used a new fundamental axiom to the effect that "Heat cannot of itself pass from a colder to a hotter body."

He also applied his results to the study of changes of state and consequent changes in volume and pressure, and deduced a number of relationships which form the basis of physical chemistry. Among others he showed that saturated vapours, when working expansively at ordinary temperatures, tend to become partially liquefied, that the difference of the specific heats is the same for equal volumes of all gases at the same temperature and pressure, and that the specific heat of a perfect gas is independent of the density. Some of these relations had, however, been proved by Carnot. In this paper Clausius also showed what conception must be formed of latent heat. "We distinguish," he writes, "in the quantity of heat which must be imparted to water during its changes, the *free* and the *latent* heat. Of these, however, we may consider only the former as really present in the vapour that has been formed. The latter is not merely, as its name implies, *concealed* from our perception; it is *consumed* during the changes, in doing work." This work Clausius correctly attributed to the "work done in overcoming the mutual attractions of the particles of the water and in separating them to such a distance that they are in the state of vapour."

Independently of Clausius, however, Kelvin by 1851

arrived at the true theory, and in a great paper on *The Dynamical Theory of Heat*, whilst admitting that Clausius had anticipated him, he placed the new science of thermodynamics on a perfectly secure foundation, free from any doubtful assumptions and developed it to such an extent that little beyond verification of his results was left to his contemporaries. He based his work on the following two propositions—the enunciation of which is his:—

“ Prop. I. (Joule).—When equal quantities of mechanical effect are produced by any means whatever from purely thermal sources, or lost in purely thermal effects, equal quantities of heat are put out of existence or are generated.

“ Prop. II (Carnot and Clausius).—If an engine be such, that when it is worked backwards, the physical and mechanical agencies in every part of its motions are all reversed, it produces as much mechanical effect as can be produced by any thermo-dynamic engine, with the same temperatures of source and refrigerator, from a given quantity of heat.”

The first proposition he regarded as proved by Joule's researches, the second he showed could be proved from the following axiom, which is one of the forms of the Second Law of Thermodynamics: “ It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.” The proof he gives is similar to that given by Clausius, and involves the consideration of another engine more efficient if possible than a reversible one, which drives the reversible one backwards making it restore to the source what it received itself. Since the more efficient engine converts a larger portion of the heat received from the source into work than would a reversible one, the reversible one working backwards could only restore the source to its original condition by taking more heat from the refrigerator than the more efficient engine gave up there, and this is contrary to experience.

In this paper Thomson also obtained the expression for the efficiency of an engine working in a Carnot cycle taking in heat Q_1 at temperature T_1 and giving up heat Q_2 at temperature T_2 as—

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_2} = \frac{W}{JQ_1},$$

the temperatures being measured on a perfect gas scale and W being the work done.

This expression enabled Thomson to modify his previous ideas as to the mode of defining temperature in an absolute way. We have seen how his first suggestion led to a scale of temperature very different from that given by the gas thermometer. On this occasion he proposed that the difference of temperature between two bodies should be defined by means of the above equation, expressing the efficiency of a Carnot engine working between these two temperatures. Then if one of them has any assigned arbitrary value that of the other follows immediately. It then became of importance to see whether the gases usually used in thermometry were sufficiently perfect to give the same value for the temperature as that derived from the thermodynamic definition, as they should do if their internal energies were unaffected by change of volume at constant temperature. The experiments to test this, which were carried out by Joule and Thomson, are described in a series of papers to the Royal Society from 1852 to 1862 on *The Thermal Effects of Fluids in Motion*. The experiments of Joule previously mentioned had indicated that the air behaved practically as a perfect gas, but his apparatus was not sufficiently refined to show deviations which would have affected its use as a thermometric substance.

Thomson suggested that the gas under examination should be forced under pressure through a porous plug, and observations of temperature made in the steady stream on each side. Air, oxygen and nitrogen showed a slight cooling effect on passing through the plug; hydrogen, however, showed an extremely small rise in temperature. The general result of the experiment then proved that the gas scale was practically coincident with the absolute or thermodynamic scale, particularly if hydrogen were used.

Before leaving the subject of thermodynamics there is another aspect to which attention was drawn by Thomson. Although the experiments of Joule had shown that energy is never created but only transformed, and that the total energy of a finite isolated system is constant, the

availability of this energy is constantly diminishing. Only in a reversible process is it possible to retransform an amount of heat energy back to its original condition. Through the agency of friction and imperfections in the methods of transforming energy, the processes available to mankind fall far short of this criterion, and every transformation involves the "dissipation" of energy. This energy takes the form of diffused heat, so that after a time, considerable, no doubt, but nevertheless finite, the whole of the energy of the solar system (considered as a finite isolated system) will have become degraded to heat at a constant temperature, and as such be unavailable for further transformation, or as Thomson writes: "Within a finite period of time past, the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject."

This idea was expressed mathematically by Clausius a few years later by the introduction of the conception of entropy. In 1854 in a paper *On an Altered Form of the Second Law of the Mechanical Theory of Heat* he investigated the properties of a function which he at first called "Aequivalenzwerth" and later "Entropy." This function is the quotient of the quantity of heat received or given out, and the absolute temperature at which the transfer takes place. If a body receive a quantity of heat at a temperature T it is said to receive entropy $\frac{Q}{T}$. In the case of a reversible cycle, the expression given above for the efficiency of a Carnot cycle leads to the equation—

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

so that there is no change in entropy. In the conduction of heat between bodies at different temperatures T_1 and T_2 one loses entropy $\frac{Q}{T_1}$ and the other gains entropy $\frac{Q}{T_2}$ which is greater. Now in actual engines and natural processes there is always friction and conduction between

bodies at different temperatures, so that there is always gain of entropy. From these considerations Clausius stated the dissipation or loss of availability of energy was due to the tendency of the entropy of the solar system towards a maximum.

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CHAPTER IX

THE KINETIC THEORY OF MATTER

THE idea of ultimate particles of matter identical in magnitude for the same substance, is one that has been referred to and discussed in several of the preceding chapters. Except as regards its application to the determination of the relative weights of the ultimate particles, the conception, so far as we have considered it, has been wholly qualitative. The development of the mechanical theory of heat, in which heat is regarded as a form of energy, naturally led to quantitative enquiry as to the physical characteristics of the ultimate holders of this energy. In consequence we find immediately following the publication of the epoch-making papers of Joule, Clausius and Thomson, a revival of interest in the discontinuous theory of the nature of matter. Even apart from the speculations of the early Greek philosophers, this idea of accounting for the physical properties of bodies in terms of the motions and masses of their small constituents was not new.

Robert Hooke (1635-1703) appears to have anticipated the modern theory in 1678 in his *Lectures de Potentia Restitutiva, or of Spring*, as the following passage shows: "The air then is a body consisting of particles so small as to be almost equal to the particles of the Heterogeneous fluid medium encompassing the earth. It is bounded but on one side, namely, towards the earth, and is indefinitely extended upward being only hindered from flying away by its own gravity (the cause of which I shall some other time explain). It consists of the same particles single and separated, of which water and other fluids do, conjoyned and compounded, and being made of particles exceeding small, its motion (to make it balance with the rest of the

earthy bodies) is exceeding swift, and its Vibrative Spaces exceeding large, comparative to the Vibrative Spaces of other terrestrial bodies. I suppose that of the Air next the Earth in its natural state may be 8000 times greater than that of steel, and above a thousand times greater than that of common water, and proportionably I suppose that its motion must be eight thousand times swifter than the former, and above a thousand times swifter than the latter. If, therefore, a quantity of this body be inclosed by a solid body, and that be so contrived as to compass it into less room, the motion thereof (supposing the heat the same) will continue the same, and consequently the Vibrations and Occursions will be increased in reciprocal proportion, that is, if it be condensed into half the space the Vibrations and Occursions will be double in number: If into a quarter the Vibrations and Occursions will be quadruple, etc. . . . These explanations will serve *mutatis mutandis* for explaining the Spring of any other Body whatsoever."

Daniel Bernoulli (1700-1782), in his *Hydrodynamica*, explained the pressure of the air as being due to the impact of air particles against any surface presented to it. This idea was also taken up by Le Sage (1724-1803), Prevost (1751-1839), Herapath (1796-1867) and Joule (1818-1889). The latter, in 1848, made calculations to determine the velocity of the particles of hydrogen which would be required to account for the observed pressure. "Let us suppose," he writes, "an envelope of the size and shape of a cubic foot to be filled with hydrogen gas, which, at 60° temperature and 30 inches barometrical pressure, will weigh 36.927 grains. Further, let us suppose the above quantity to be divided into three equal and indefinitely small elastic particles, each weighing 12.309 grs.; and further, that each of these particles vibrates between opposite sides of the cube, and maintains a uniform velocity except at the instant of impact; it is required to find the velocity at which each particle must move so as to produce the atmospherical pressure of 14,831,712 grs. on each of the square sides of the cube. In the first place, it is known that if a body moving with the velocity of $32\frac{1}{6}$ feet per second be opposed during one second, by a pressure equal to its weight, its motion will be stopped, and that, if the pressure be continued one second longer, the particle will

acquire the velocity of $32^{1/6}$ feet per second in the contrary direction. At this velocity there will be $32^{1/6}$ collisions against each side of the cubical vessel every two seconds of time; and the pressure occasioned thereby will be $12.309 \times 32^{1/6} = 395.938$ grs. Therefore since it is manifest that the pressure will be proportional to the square of the velocity of the particles, we shall have for the velocity of the particles requisite to produce the pressure of 14,831,712 grs. on each side of the cubical vessel,

$$u = \sqrt{\left(\frac{14,831,712}{395.938}\right)} 32^{1/6} = 6225 \text{ feet per second.}$$

“The above velocity will be found equal to produce the atmospheric pressure, whether the particles strike each other before they arrive at the sides of the cubical vessel, whether they strike the sides obliquely, and, thirdly, into whatever number of particles the 36,929 grs. of hydrogen are divided.”

Analytically the above result is expressed by the equation $u^2 = 3p/\rho$, i.e. $p = \rho u^2/3$ where p is the pressure and ρ is the density, or by $pv = Mu^2/3$ where M is the mass occupying a volume v .

It is to Clausius (1822-1888) that we are indebted for the first serious attempt to found a kinetic theory of matter, in a paper entitled, *Ueber die Art der Bewegung, welche wir Wärme nennen*, published in 1857. He considered a gas to be a collection of molecules travelling about in all directions with very high velocities, and deflecting each other from their rectilinear paths on approaching within a very small distance from each other. He assumed the time during which the encounters took place was very short and that the collisions could be considered as between perfectly elastic bodies. From these considerations he showed that the gas laws could be deduced, for if the pressure of a gas were regarded as due to the sum of the impulses given by the molecules in striking the walls of the envelope, doubling the amount of gas would double the number of impulses and so double the pressure, and thus the pressure is proportional to the density—which is Boyle's Law. Similarly, if the heat content of a gas were regarded as “the *vis viva* of its molecular motions” and proportional to the

absolute temperature, a given proportionate increment of temperature would produce the same proportionate increment of pressure, if the volume were kept constant, since both are proportional to the square of the velocity of the molecules (i.e. the *vis viva*), and this is Charles' Law.

Clausius also showed that the slowness of diffusion of gases, in spite of the enormous velocities which the molecules possessed, was a result of the innumerable collisions they experienced, which by constantly changing their directions of motion tended to prevent any rapid separation of particles originally close together.

As a result of reading Clausius' memoirs on the kinetic theory, James Clerk Maxwell (1831-1879) became interested in the subject, and immediately deduced results of very great importance. Clausius in his mathematical treatment of the motions of the molecules assumed that they all possessed the same velocity, although he knew that the velocity of a molecule must vary between very wide limits. Maxwell at once sought for a law to express the distribution of the velocities of the particles. As it is obviously impossible to follow the behaviour of individual molecules he introduced the theory of probability, and showed that if it be assumed there is a constant distribution of velocities about the mean in spite of the rapidly changing velocities of individual molecules, the law giving the distribution, is of "exactly the same mathematical form as the distribution of observations according to their errors, as described in the theory of errors of observation. The distribution of bullet-holes in a target according to their distances from the point aimed at, is found to be of the same form, provided a great many shots are fired by persons of the same degree of skill." He also showed how the viscosity of a gas depended on the mean free path (i.e. the average length of path of the molecules between successive collisions), and deduced the unexpected result that the viscosity of a gas was independent of the pressure. This result was tested and confirmed by determining the rate at which a disc performing torsional oscillations in a horizontal plane, came to rest when immersed in air at different pressures. Maxwell's first paper on this subject, in 1860, was based on the assumption of elastic spherical molecules, but his experiments on the viscosity of air at different temperatures led

him to the conclusion that it varied in a way contrary to this assumption, and more in accordance with the assumption that the molecules repelled each other with forces varying as the inverse fifth power of the distance. This law of force simplified the calculations with regard to viscosity, diffusion and conduction of heat through gases which involved consideration of the nature of collisions, for with this law of force the number of encounters of any kind was independent of the temperature (i.e. the velocity) of the molecules.

He deduced a number of important results which were quite independent of the law of force between the molecules. The first is the condition of equilibrium of mixed molecules of unequal mass, viz. that the mean energy of translation of the molecule is the same whatever its mass. When gases are mixed we know that in equilibrium there exists a constant temperature throughout the mixture, so that the physical significance of the equality of temperature of two gases is that the mean energies of translation of their molecules are the same. Now in the case of two separate gases under the same conditions of temperature, pressure and volume, the equality of temperature demands that the *mean* energy of translation should be the same, while the equality of pressure demands that the *total* energy of translation per unit volume should be the same in each gas. Hence the number of molecules per unit volume is the same in each gas, in agreement with Avogadro's hypothesis of 1811.

The second is the condition of equilibrium of a vertical column of mixed gases, viz. the density of each gas at any point is the same as if no other gas were present. This is the same distribution as was given by Dalton for the equilibrium of a mixed atmosphere.

The third is the condition of equilibrium in a vertical column of gas, viz. that the temperature throughout is constant, and hence that temperature is independent of height in all other substances.

In addition to kinetic energy of translation, it is possible for a molecule to have energy as a result of the motion of its internal parts, such as rotations or vibrations with respect to its centre of gravity. If a molecule were a pure centre of force then there could be no rotation and the

whole energy would be energy of translation. Clausius had early recognised this, and suggested as a plausible assumption that the average values of the total energy and of the energy of translation in a given substance, tend to a constant ratio with each other, and had pointed out that if γ (i.e. the ratio of the two specific heats) were known, then the ratio of the increment of total energy to the increment in energy of translation could be determined. Maxwell investigated the distribution of the two kinds of energy in 1860, and came to the conclusion, on the hypothesis of elastic molecules of invariable form, that not only must the ratio be constant but that the energy of the internal motion must equal that due to translation. Ludwig Boltzmann (1844-1906), too, investigated this problem, and worked out the general case in which a molecule had n degrees of freedom, that is, n co-ordinates are required to specify completely its position. The position of a point is uniquely determined by three co-ordinates, while that of a rigid body needs six. He found, as Maxwell did, that the average energy of translation is the same for molecules of all kinds at the same temperature, that the ratio of the total energy to the energy of translation is as n is to 3, and that the energy associated with each co-ordinate is the same. This led to the establishment of the Maxwell-Boltzmann Law of the Equipartition of Energy in each degree of freedom.

As a result of this principle, it follows that when a gas is heated a fraction $(n - 3)/n$ of the energy received goes into internal energy, and that $3/n$ goes into energy of translation. In the case of the specific heats of gases at constant pressure and at constant volume, Maxwell showed that $\gamma = 1 + 2/n$, and in the interpretation of this equation came up against very great difficulties. Obviously a molecule in space cannot have less than three degrees of freedom, so that γ cannot be greater than 1.66, which was, however, too large for any gas known at that time. The most plausible value of n is 6 corresponding to a rigid body giving $\gamma = 1.33$, whilst Regnault's researches had shown that for air and several other gases $\gamma = 1.40$ corresponding to $n = 5$. Spectroscopic evidence, however, suggested that as a gas can give a complicated line spectrum, its constitution must be very complex, so that n should be greater

than 6, and thus increased the disparity between the calculated and observed values of γ . Somewhat later Boltzmann suggested that if a diatomic molecule consisted of a pair of atoms rigidly connected together, collisions with other molecules would not affect rotation round the axis of symmetry, and that the number of effective degrees of freedom would only be five and the value of γ obtained from the theory would agree with that actually observed for a number of diatomic gases.

Meanwhile, Clausius was attacking the problems of the kinetic theory from a different point of view. We have seen that in his early work he assumed that the time involved in a collision was small compared with that in which the molecule was describing its mean free path. In these circumstances the fraction of the total molecules of any system which at any instant are encountering others and coming under the influence of their mutual forces is very small. In 1870, in a paper *Ueber einen auf die Wärme anwendbaren Satz*, he left out this assumption and introduced his conception of the *virial*. When a stress (due to attraction or repulsion) exists between two points, half the product of the stress and the distance between the points he defined as the virial of the stress. For steady motion in a gas he deduced that

$$\sum \left(\frac{1}{2} m v^2 \right) = \frac{3}{2} p v + \sum \left(\frac{1}{2} R r \right),$$

R and r being the stress and distance between two molecules, R being positive if attractive and negative if repulsive.

In the case of gases at low pressures Boyle's Law is obeyed very exactly, but as the volume is diminished the observed pressures become less than the law requires. Now the virial depends on the number of molecules acting on each other at any instant, so that the importance of this term is increased, and since it diminishes the pressure, the stresses between molecules must be attractive. Now Andrews' (1813-1885) experiments on carbon dioxide at temperatures below 31° C. showed that if the volume were reduced to a certain volume, liquefaction began, and that the pressure would remain constant until all the gas had liquefied. The result of further compression is to increase

the pressure very much more than Boyle's Law indicates so that, in this case, the virial is negative, that is to say there is a repulsive force between the molecules. For carbon dioxide above 31°C . or any other gas above its critical temperature, there is no liquefaction, and the virial merely changes sign from positive to negative when a certain degree of compression is reached.

From this conception of the virial van der Waals (1837-1923), in 1873, in his celebrated memoir *On the Continuity of the Liquid and Gaseous States*, deduced a corrected form of Boyle's Law which agreed fairly well, at any rate qualitatively, with observed results. On the assumption that the temperature of a gas was proportional to the mean kinetic energy of the molecules, which he treated as elastic spheres, he showed that

$$(p + a/v^2)(v - b) = RT,$$

where a/v^2 is the molecular pressure arising from their attraction, and b is proportional to the volume of the molecules, so that $v - b$ is the "effective volume" in which the molecules can move.

As a result of the work of Clausius and Maxwell, together with experimental work on viscosity, diffusion and conduction of heat in gases by O. E. Meyer (1834-1909), and by J. Loschmidt (1821-1895), it became possible to calculate the velocities, the mean free paths, the radii and the number per cubic centimetre of the so-far hypothetical molecules. Data on the pressure and density of gases gave the velocities directly as Joule's calculation showed. The velocity obtained in this manner is that velocity which, when squared and multiplied by the mass, gives the mean *vis viva* of the molecule. In the case of hydrogen the velocity at 0°C . is about 184,000 cm. per second, and since the velocities are inversely proportional to the square root of the density, that of oxygen is about 46,000 cm. per second. Maxwell's theoretical and experimental investigations into viscosity enabled the mean free paths to be calculated. These, in the cases of hydrogen and oxygen at 0°C . and 760 mm. pressure, are about 17.0×10^{-6} cm., and 8.7×10^{-6} cm. Clausius, in 1858, had deduced a relation between the mean free path, the molecular radius

and the molecular volume of a gas, that is, the ratio of the volume of a liquid to that of the gas producing it. Loschmidt, in 1865, determined this ratio, and by means of Clausius' equation obtained for the diameter of the hydrogen and oxygen molecules 11.0×10^{-8} cm. and 6.0×10^{-8} cm. respectively. The collision frequency which can be obtained from the velocity and the mean free path, is of the order of 10^9 per second, and gives an indication of the reason why the diffusion of gases takes place so slowly.

Hitherto the kinetic theory has appeared merely in the light of a fairly satisfactory "*construierbar Vorstellung*" of the assumed invisible motions to whose action certain phenomena, and particularly those of heat, were attributed. It attained a considerable measure of success quite early in its development. The first great triumph was the prediction of the independence of the viscosity and pressure of a gas. This was followed by a similar prediction in the case of the heat conductivity of a gas, which the theory showed should be independent of the density. The difficulty of the maximum value of the ratio γ , previously mentioned, was removed shortly afterwards by Kundt (1838-1894) and Warburg (b. 1846) in 1876, who showed that for mercury vapour this ratio was 1.66, indicating on the kinetic theory that its molecules have only three effective degrees of freedom, so that they must be monatomic and act like pure centres of force. There was considerable doubt as to what was a degree of freedom in molecular systems. The spectroscopic evidence suggested the possession of many degrees of freedom, which on that theory should make γ approximately equal to unity.

The values given by Loschmidt, Meyer and others for the molecular constants showed that the molecules were far too small to be seen by any microscope, for the molecular radius, as we have seen, was found to be less than one-tenth the wave-length of yellow light.

The first direct evidence of the existence of molecules was provided by the phenomena occurring in fairly high vacua. Sir William Crookes (1832-1919) discovered that a paddle-wheel consisting of mica vanes, blackened on one side and pivoted in an evacuated glass vessel, revolved

when brought near to a source of heat. Maxwell explained this phenomenon as being due to the stresses set up in a rarefied gas owing to inequalities of temperature. He showed that with a gas in this condition the pressure is not the same in all directions, and that when the density of the gas is small enough the stresses set up may be of considerable magnitude. It is easy to see that the blackened sides of the vanes absorb more heat than the unblackened sides, and in consequence molecules rebounding from them receive an increase in their kinetic energy, so that the average kinetic energy of the reflected molecules from the blackened sides is somewhat greater than that of those reflected from the unblackened sides. This is equivalent to a pressure acting on the vane, which in consequence revolves unblackened side foremost.

The kinetic theory also received substantial confirmation from the work of van't Hoff (1852-1911) on the osmotic pressure of dilute solutions. This phenomenon was first described by the Abbé Nollet (1700-1770), who found that if a glass vessel filled with spirits of wine and having its opening closed by an animal membrane, were immersed in water, the water passed through the membrane and developed a pressure inside the glass vessel, so that the membrane dilated and often burst. The German botanist Pfeffer (1845-1920) investigated this phenomenon experimentally in 1877, and measured the osmotic pressure (as it was called) for several solutions. He also found how the pressure varied with the concentration of the solution and with the temperature, and showed that in the former case it was proportional to the concentration so long as this was not too great, and that in the latter it was proportional to the absolute temperature.

In 1887 van't Hoff demonstrated how the phenomena of osmosis were such as one would expect if the molecules of the dissolved substance played the part of an ideal gas. In support of his theory he showed that Pfeffer's observation on the variation of osmotic pressure with concentration was really Boyle's Law applied to these molecules, and that the results on the variation with temperature led to Charles' Law, while the additional observation that the osmotic pressures due to concentrations proportional to the molecular weight of the solutes were equal, indicated

that equal volumes of dilute solutions exerting the same osmotic pressure contain the same number of molecules of solute.

He further deduced that not only are these numbers equal to each other, but they are equal to the number of molecules in the same volume of a perfect gas at the same pressure and temperature, and so laid the foundations of a kinetic theory of dilute solutions, obeying the same laws as the gas laws. Since the molecules in a dilute solution behave in many respects like the molecules of a gas, it is obviously possible to consider a dilute solution as the working substance in a Carnot cycle. This was done by van't Hoff, who thus deduced many general relationships, such as the lowering of the vapour pressure of a solvent by the presence of a solute. The joint application of the kinetic theory and of thermodynamics has proved of great utility in elucidating the laws and conditions of equilibrium in chemical reactions, and has led to the development of that very vigorous branch of science known as Physical Chemistry.

The most direct evidence as to the actual existence of molecules was obtained from the study of the Brownian motion. The British botanist, Robert Brown (1773-1858), in 1827 noticed the continual, rapid and irregular motion of particles of pollen suspended in a liquid. The phenomenon is seen if any sufficiently small particles suspended in a liquid or gas are viewed with a microscope. These motions were the subject of considerable study, and in 1879 Ramsay showed that they were probably due to the bombardment of the particles by the molecules of the liquid in which they were suspended. The French physicist Gouy (1864-1926) arrived independently at the same conclusion in 1888, as he proved the motion was independent of the light by which it was viewed, and that it was not due to convection currents or to external vibration. Over surfaces of large area the total pressures due to bombardments are constant, and no motion is to be expected; if, however, the surface is of the same order of magnitude as the mean free paths of the molecules of the liquid, then variations in pressure and consequent motion are to be expected, on account of the probable variations in the number of bombarding molecules incident on the surface per second.

It is largely to Jean Perrin that the quantitative treatment of this phenomenon is due. The following extract from his book, *Brownian Movement and Molecular Reality* (1910), gives in a very clear manner the way in which his experiments form a test of the kinetic theory and of the principle of the equipartition of energy:—

“We have seen,” he writes, “that the mean molecular energy is, at the same temperature, the same for all gases. This result remains valid when the gases are mixed. . . . This invariability of molecular energy is not confined to the gaseous state, and the beautiful work of van’t Hoff has established that it extends to the molecules of all dilute solutions. . . . It therefore follows that the molecular energy is the same in a liquid as in a gas, and we can now say:—

“At the same temperature all the molecules of all fluids have the same mean kinetic energy, which is proportional to the absolute temperature.

“But this proposition, already so general, can be still further enlarged. According to what we have just seen the heavy molecules of sugar, which move in an aqueous sugar solution, have the same mean kinetic energy as the lighter molecules of water. These sugar molecules contain 45 atoms; the molecules of sulphite of quinine contain more than 100 atoms, and the most complicated and heaviest molecules to which the laws of van’t Hoff can be extended may be cited. The applicability of the generalisation does not appear to be limited to any *size* of molecule. Let us now consider a particle a little larger still, itself formed of several molecules, in a word, a speck of dust. Will it proceed to re-act towards the impacts of the molecules encompassing it according to a new law? Will it not comport itself simply as a very large molecule, in the sense that its mean kinetic energy has still the same value as that of an isolated molecule? This cannot be averred without hesitation, but the hypothesis is sufficiently plausible to make it worth while to discuss its consequences. Here we are then taken back again to the observation of the particles of an emulsion, and to the study of this wonderful movement which most directly suggests the molecular hypothesis. But at the same time we are led to render the theory precise by saying, not only that each particle

owes its movement to the impacts of the molecules of the liquid, but further that the energy maintained by the impacts is on the average equal to that of any one of these molecules. . . . So that if we find a means of calculating this granular energy in terms of measurable magnitudes, we shall have at the same time a means of proving our theory."

This Perrin was able to do from observations on the distribution of the particles under the action of gravity. The particles distribute themselves according to the same law that regulates the density of the isothermal atmosphere, so that the number of particles per unit volume and the pressure are greatest at the bottom. The difference of pressure between any two planes then balances the gravitational attraction on the particles between the planes. The difference in pressure can be expressed as a function of known quantities and the mean kinetic energy of a particle. The gravitational attraction can be found from a knowledge of the size and density of the particles. Perrin then deduced the value of the Avogadro constant, i.e. the number of molecules in a gram molecule. The mean of his results was about 68.5×10^{22} which agreed very satisfactorily with results obtained by other methods, thus providing an excellent proof of the fundamental accuracy of the assumptions of the kinetic theory.

Before leaving the subject of thermodynamics, it will be useful to indicate how the results of the kinetic theory have an important bearing on Thermodynamics and the conception of Entropy. The two laws of Thermodynamics rest on very different foundations. The first expresses the experimental fact that any amount of work can be transformed into an equivalent amount of heat while the second merely expresses our limitation to bring about the reverse transformation, except in a certain definite ratio determined by the temperatures of the bodies acting as vehicles of the heat, whereas on purely mechanical principles we should expect complete retransformation to be possible. Maxwell, in his *Theory of Heat*, points out that this is due to the fact that human beings cannot control the motions of the individual molecules whose energy represents the heat content of bodies on this theory—that, in fact, the axiom from which Thomson deduced the law of the dissipation

of energy results from the rudeness of the mechanism by which we regulate these movements. "One of the best established facts in thermodynamics," he writes, "is that it is impossible in a system enclosed in an envelope which permits neither change of volume nor passage of heat, and in which both the temperature and the pressure are everywhere the same, to produce any inequality of temperature or pressure without the expenditure of work. This is the second law of thermodynamics, and it is undoubtedly true so long as we can deal with bodies only in mass and have no power of perceiving or handling the separate molecules of which they are made up.

"But if we conceive a being whose faculties are so sharpened that he can follow every molecule in its course, such a being whose attributes are still as essentially finite as our own would be able to do what is at present impossible to us. For we have seen that the molecules in a vessel full of air at uniform temperature are moving with velocities by no means uniform, though the mean velocity of any given number of them, arbitrarily selected, is almost certainly uniform. Now let us suppose that such a vessel is divided into two portions, A and B, by a division in which there is a small hole, and that a being, who can see the individual molecules, opens and closes this hole so as to allow only the swifter molecules to pass from A to B, and only the slower ones to pass from B to A. He will thus, without the expenditure of work, raise the temperature of B and lower that of A, in contradiction to the second law of thermodynamics."

Thus for Maxwell's "demon" the second law of thermodynamics does not hold. But there is nothing to prevent such a sorting out of the molecules into two classes occurring naturally since the movements of the molecules are controlled by chance, subject to the condition that the sum total of their energies is constant, though there is an immense probability against such an event happening in any finite time just as, borrowing an analogy from Jeans, there is a very large probability against a dealer in a game of cards dealing thirteen trump cards in one hand to a single player. The explanation is that a hand of thirteen trumps can only be dealt in relatively few ways, while a mixed hand can be dealt in a very large number of ways.

The further development of the idea of probability in thermodynamics is due to Boltzmann who applied it to the study of entropy about 1877. For a given system containing a number of molecules whose total energy is constant, it is possible to calculate the probability of any given arrangement or "complexion" of the molecules as regards their positions and velocities with reference to a standard state in which they are equally spaced, and all have the same velocity. The standard complexion is, however, impossible to maintain, even if we could start with it, for owing to collisions, any ordered arrangement of molecules would very quickly disappear, and a completely chaotic state or a maximum "mixed-up-ness" would result. On the attainment of this state all reason for a further change would vanish, so that Boltzmann regarded complete "mixed-up-ness" as the condition for thermal equilibrium. Now we know that with bodies at different temperatures in an envelope such as that mentioned by Maxwell above, thermal equilibrium would in time occur, and our previous consideration of the result of interchange of heat between bodies at different temperatures has shown that the entropy would increase to the maximum value compatible with the fixed condition that the total energy is constant. It is thus obvious that there is a close connection between the thermodynamic probability and the entropy of a system. Since the total entropy of a mixture of two complexions is the sum of the entropies, while the probability of the mixture is the product of the separate probabilities it follows that $S = k \log W$, where S is the entropy, W the probability, and k a constant, independent of the nature of the system.

The work of Boltzmann in thus bringing the concept of entropy into the domain of statistical mechanics has since been followed by that of Planck (b. 1858) who, by means of somewhat similar considerations applied to elements of physical disturbance, has been able to construct an abstract system of thermodynamics, and by applying it to the problem of radiation has confronted the scientific world with the problem of the quantum with which, however, we shall deal in a later chapter.

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CHAPTER X

RADIATION

THE problem of the transference of heat by radiation was first investigated by Newton. Though he favoured the corpuscular view as to the nature of light, yet he maintained that the radiation of heat was due to a vibration in an æther. In the queries at the end of his *Opticks* he writes: "And do not hot Bodies communicate their Heat to contiguous cold ones, by the Vibrations of this Medium propagated from them into the Cold ones? And is not this Medium exceedingly more rare and subtile than the Air, and exceedingly more elastick and active? And doth it not readily pervade all Bodies? And is it not (by its elastick force) expanded through all the Heavens?"

Newton, in 1701, made experiments on the rate of cooling, and found that it was proportional to the excess of temperature above the surroundings, that is to say, during equal intervals of time the same proportionate change in the excess of temperature took place. This law is not strictly true, however, and can only be used in cases where the excess temperature is small. Newton determined this law in order to estimate high temperatures, such as that of a red-hot iron ball, from observations on the time taken in cooling through known temperatures. Its application without restriction led to very erroneous results: thus Herschel on the assumption that its heat radiation varies directly as the excess temperature found a value for the temperature of the sun nearly a thousand times too high.

The next advance in our knowledge of radiation was due to Prevost (1751-1839), who in 1791 enunciated the theory of exchanges. Pictet (1752-1825) had shown that a thermometer at the focus of a concave mirror indicated a fall

of temperature when placed opposite a similar mirror having a piece of ice at its focus. The simplest explanation of this phenomenon, is that "*cold*" is something capable of being radiated. It was due to Prevost's conviction of the inadmissibility of this explanation that he was led to the theory of "a moveable equilibrium of temperature." The main idea of his theory is that all bodies, hot or cold, are constantly radiating heat to one another, and that constancy of temperature occurs when a body radiates just as much as it receives from other bodies. Thus if a temperature difference is set up by any means, the inequality of the resulting heat exchanges tends to restore the equilibrium of temperature.

In 1800 Sir William Herschel (1738-1822) discovered the existence in the solar spectrum of invisible rays which possessed considerable heating properties. He noted the temperature of a thermometer when placed in different parts of the solar spectrum, and showed that the heating effect of the radiation increased towards the red end of the spectrum, and that instead of terminating there continued well beyond. This indicated the existence of "dark" rays in addition to light rays in the radiation of the sun. Within a year Ritter (1776-1810) discovered "dark" rays at the other end of the spectrum, beyond the violet, which had the property of blackening nitrate of silver. As we have seen in Chapter VI, the work of Young, Fresnel and Arago showed that light was a wave motion in the luminiferous æther, so that when this theory became generally accepted it was natural to identify the heat rays and chemical rays with light rays, differing from visible light merely in wave-length and frequency of vibration.

These discoveries of Herschel and Ritter opened up an entirely new field of activity. The heat rays were subjected to investigation by many workers, notably Leslie (1766-1832), Forbes (1809-1868), and Melloni (1798-1854). The latter in particular between 1830 and 1840 demonstrated that the heat rays exhibited all the characteristics of visible light rays, as they could be reflected, refracted, polarised, and could also be made to show interference and diffraction effects.

A very great deal of work was done by these observers and also by Tyndall (1820-1893), Magnus (1802-1870) and

Balfour Stewart (1828-1887) on the emissive and absorptive powers of various bodies for heat radiation. It was shown that many substances which are transparent to visible light are very opaque to much of the invisible heat radiation, and that polished metals which are good reflectors are very feeble radiators when compared with dark or black bodies at the same temperature. The correct interpretation of these phenomena was only given when Balfour Stewart and Kirchhoff (1824-1887) independently in 1859 extended Prevost's theory of total heat exchanges to include the consideration of the separate components of the heat radiation.

Before considering their work, it will be well at this stage to refer to the discovery of the dark lines in the solar spectrum and their interpretation. In 1802 Wollaston (1766-1828) discovered that the spectrum of the sun was crossed by a series of dark lines. Joseph von Fraunhofer (1787-1826) rediscovered these in 1814, and examined the dark lines in great detail. He was able to distinguish about 600 of them, the most prominent of which he named after the letters of the alphabet so that they might be used as reference lines. He showed that they always appeared in the same place in the spectrum, independently of the way in which it was produced. The wave theory of light was not developed sufficiently at that time, so instead of measuring the wave-length of the various lines as we should do to-day, he determined their refractive indices in several substances, liquid and solid. Fraunhofer also noticed the coincidence of a pair of bright yellow lines seen in the spectrum of a candle flame, with the dark D lines in the solar spectrum.

No further progress was made in the study of these lines for several years. Sir John Herschel (1792-1871) in 1823 suggested that the lines which appeared in the spectrum of a flame when various metals were held in it could be used as a test of their presence in other substances, and considerable work in mapping the spectra of metallic vapours was done by many investigators in consequence. Shortly after this, it was pointed out by Foucault that the yellow lines in the spectrum of a flame which coincided with the D lines were due to sodium, while Stokes suggested that the dark lines were due to the absorption of lines of the

sun's spectrum, either by the sun's or by the earth's atmosphere by resonance, that is to say the molecular constituents of the sun's or the earth's atmosphere absorb the energy of those waves coming from the sun whose vibration period corresponds with their own.

The correct explanation of the dark lines was given by Kirchhoff in 1859. At that time he was working in collaboration with the German chemist Bunsen (1811-1899) in determining the spectra of the elements. "In order," he writes, "to test in the most direct manner possible the frequently asserted fact of the coincidence of the sodium lines with the lines D of Fraunhofer, I obtained a tolerably bright solar spectrum, and brought a flame coloured by sodium vapour in front of the slit. I then saw the dark lines D (of the solar spectrum) change into bright ones. The flame of a Bunsen's lamp threw the bright sodium lines upon the solar spectrum with unexpected brilliance. In order to find out the extent to which the intensity of the solar spectrum could be increased without impairing the distinctness of the sodium lines, I allowed the full sunshine to shine through the sodium flame, and to my astonishment I saw that the dark lines D appeared with an extraordinary degree of clearness." That is, the dark lines appeared darker than in the ordinary solar spectrum. This suggested to him that the sun's rays might have passed through sodium vapour at some other point in their path before reaching the earth. To verify this hypothesis, he passed the light from an oxy-hydrogen lime-light through a sodium flame, and found that instead of the usual continuous spectrum of the lime-light he got two dark bands coinciding with the D lines. The introduction of potassium, strontium, iron, etc., produced dark lines corresponding to those in the solar spectrum. Finally, he did the same with lithium, which gives a bright red line without a corresponding one in the solar spectrum. On passing a beam of sunlight through the lithium flame a dark line appeared at the expected place, thus showing that the incandescent gas absorbs those rays which it emits.

The explanation of this important discovery is to be found in the extension of Prevost's theory of exchanges by both Kirchhoff and Balfour Stewart independently in 1859, through considerations based on the equilibrium of the full

or complete radiation in a constant temperature enclosure. Prevost's theory only applied to the total radiation in such an enclosure, and stated nothing with regard to the composition of such radiation. The following quotation from Balfour Stewart's *Elementary Treatise on Heat* gives in an admirable manner the main line of the argument: "We have seen that the stream of radiant heat which strikes upon the thermometer in our enclosure of constant temperature is independent both of the materials and of the shape of the walls of the enclosure, so that if the instrument be carried from one part to another, there will be no change in the amount of radiant heat falling upon it. Something more, however, is necessary, for we must not only have the *quantity* of heat which falls upon the thermometer the same throughout, but the *quality* of this heat must also be the same." . . . "Now the word 'quality' is here taken to denote *any specific peculiarity, whether of wave-length or polarisation*, which causes rays of heat to be differently absorbed by any substance. . . .

"Suppose now that our thermometer is covered with some substance which displays this selective absorption for certain kinds of heat, and that we carry it about from one part of the enclosure to another. It will not only be necessary that the *quantity* of radiant heat which beats upon our thermometer shall be the same throughout the enclosure, in order that the instrument may preserve its constancy of temperature, but the *quality* of this heat must also be the same; for if not, we might suppose that in one place the heat is of a kind that is greedily absorbed by the coating of the bulb, and that in another place it is of a kind that is reflected back from this coating; thus although the quantity of heat falling on the bulb might be the same in both places, yet the thermometer would absorb more in the first place than in the second, and its constancy of temperature would be destroyed. It is therefore clearly necessary that the stream of radiant heat which beats against the thermometer as it is carried about in the enclosure, should be the same at all places, both as to *quantity* and *quality*. . . . Such a surface (the coating of the thermometer) must not only give back by radiation to the general stream of heat as much as it withdraws by absorption, but what it gives back must be of the same quality as that which it withdraws."

Kirchhoff treated the question mathematically, and deduced that the ratio of the absorptive and emissive powers of all bodies for any given wave-length is the same at the same temperature. Stewart and Kirchhoff gave a number of striking examples of the relation between emission and absorption in various substances. They showed that tourmaline absorbs radiation polarised in a certain plane and that the radiation emitted by heated tourmaline is polarised in the same plane, while Stewart showed that rock salt which is very transparent to heat rays is very opaque to the radiation from another piece of heated rock salt.

These considerations then established that the "full" or "black body" radiation at any temperature in a constant temperature enclosure is independent of the materials of the enclosure, and only depends on the temperature; that if a body at any temperature absorbs a particular kind of radiation, it must also emit the same kind of radiation at the same temperature; and that if it is placed in a constant temperature enclosure the emission and absorption must be equal.

Kirchhoff immediately extended his explanation of the dark lines in the solar spectrum by showing that the absorption was due to the passage of rays from the hotter portions of the sun through the cooler envelope, and that in these conditions, the temperatures being different, the emission of the cooler parts was not equal to their absorption, and so the dark lines were places of relative darkness compared with the rest of the spectrum. As a result it became possible to correlate any dark line in the solar spectrum with the presence in the sun's atmosphere of those terrestrial substances which had corresponding bright lines in their incandescent spectra. This led to the rapid development of spectroscopic astronomy which, through the labours of Huggins (1824-1910), Janssen (1824-1907) and Lockyer (1836-1920), has enabled a large amount of information relative to the constitution, physical condition, and even the motions of stars and nebulae to be obtained.

The conception, due to Stewart and Kirchhoff, of full or black body radiation solely as a function of the temperature, led to a very active study of the connection between radiation and temperature. Stefan (1831-1897), in 1879, deduced an empirical relationship from a consideration of

some results of Tyndall's on the loss of heat from hot wires. The temperatures of the wires were not known very accurately, but they sufficed to show that the total radiation between two bodies varied as the difference of the fourth powers of their respective absolute temperatures. He also found that this law agreed with the experiments of Dulong and Petit (1817) on the rate of cooling of a thermometer in an exhausted vessel. This law is usually referred to as Stefan's Law, and is expressed by the equation

$$R = \sigma(T_1^4 - T_2^4)$$

where R is the radiation from a body at absolute temperature T_1 to a body at temperature T_2 and σ is a constant.

Further development in our knowledge of radiation next occurred as a result of the application of the theoretical deduction by Maxwell in 1873 that a beam of light should exert a mechanical pressure on a surface.

Maxwell had shown that when a plane electromagnetic wave falls on a perfectly absorbing surface a mechanical pressure is exerted on unit area equal to the energy contained in unit volume of the wave. Experiments by Lebedew (1866-1912), in 1900, and by Hull (b. 1870) and Nicholls (1870-1924) in America a few months later, verified the existence of this pressure. The latter investigators also showed that it agreed quantitatively with Maxwell's theory, in direct disagreement with the numerical value of the pressure deduced on the corpuscular theory of light. As a consequence of this mechanical pressure it is possible to consider radiation as the working substance in a Carnot cycle.

This fruitful conception was due to Bartoli (1851-1896), who in 1875 showed how otherwise an arrangement could be conceived which, by means of the compression of radiation, would transfer heat from a colder to a hotter body. He considered a cylinder having perfectly reflecting sides, closed at each end by portions of "black bodies," or perfect absorbers at different temperatures, and having a moveable perfectly reflecting partition in the middle. By imagining another reflecting piston to move from the body at the lower temperature, and so to compress a portion of radiation initially in equilibrium with this body, the energy density of the radiation between the piston and partition is increased, and on sliding away the partition some of it is

absorbed by the body at the higher temperature. By the second principle of thermodynamics this is impossible unless mechanical work is done in the operation, which work can have resulted only from the movement of the piston against the pressure of the radiation.

In 1884 Boltzmann (1844-1906) took up the radiation problem, and applied the method of treatment which had been indicated by Bartoli. By considering an enclosure containing full radiation corresponding to a definite temperature and subjecting it to a cycle of isothermal and adiabatic changes, he proved that the energy of full radiation per unit volume should be proportional to the fourth power of the absolute temperature or $R = \sigma T^4$. This law has been verified by a number of observers, notably by Lummer (1860-1925) and Pringsheim (1859-1917) in 1897 and by Kurlbaum (b. 1857) in 1898 who, employing an aperture in an enclosure of constant temperature, and comparing the emitted radiation at different temperatures from 190°C. to 2300°C. by means of a bolometer, obtained very good agreement with the theory. These results have since found an extensive application in the measurement of high temperatures, for if the total radiation from a source at a known temperature be determined, measurement of the total radiation at any other temperature enables that temperature to be determined.

The variation of the quantity of full radiation with temperature having been determined, efforts were then made to discover how the quality or composition of full radiation varied with temperature. The work of Tyndall, Langley (1834-1905) and others, had shown that in addition to the increase of energy in each wave-length which occurred with rise of temperature, the proportionate increase was greater in the shorter wave-lengths than in the longer ones, so that the wave-length which had the greatest energy suffered a displacement in the direction of shorter wave-length. Wien (b. 1864) in 1893, in the deduction of his "displacement law" made an important step towards the solution of this problem. Balfour Stewart in 1871 had suggested that the movement of a body inside a constant temperature enclosure would produce the Doppler-Fizeau effect in the radiation, that is, the constituents of the reflected radiations would differ in period from the incident radiations.

Wien considered the behaviour of complete radiation when enclosed in a perfectly reflecting spherical enclosure and subjected to an adiabatic compression. In such an enclosure any arbitrary distribution of radiation will persist so long as the volume of the enclosure is not altered. He then showed that in an adiabatic change produced by a uniform shrinking of the enclosure, the effect of the reflections from moving walls was to alter all the frequencies or wave-lengths of the constituents of the radiation so that the new radiation corresponded to full radiation at some other temperature. In addition, Wien showed that all the wave-lengths were altered in a common ratio, and that the intensities were changed so that the curves showing the distribution in intensity at the various wave-lengths for the temperatures between which the compression was made, were of the same form, namely,

$$E_{\lambda}d\lambda = c^2\lambda^{-5}F(\lambda T/c)d\lambda$$

where E_{λ} is the energy at wave-length λ , c is the velocity of light, and F is an undetermined function.

From this equation it can be deduced that the wave-length which has the maximum energy varies with the temperature in accordance with the very simple relation, $\lambda_{\max} T = \text{Constant}$, which is usually referred to as Wien's Displacement Law. Hence if this constant is determined by measurements at one temperature, the "displacement" of the wave-length of maximum energy at any new temperature may be determined, or the temperature may be deduced from the displacement.

These relationships were tested experimentally by Lummer and Pringsheim in 1899 and by Paschen (b. 1865) in 1901, and a fairly accurate verification of the theory resulted. Thus the problem of determining the energy distribution in the spectrum of a black body was reduced to the determination of the form of the function $F(\lambda T)$. Thermodynamical reasoning has not been able to afford any further information. Wien determined the form of this function by the introduction of the results of the kinetic theory on the probability distribution of velocities. He considered that in a constant temperature enclosure containing a gas whose molecular kinetic energies were

distributed according to the Maxwellian Law, those molecules whose kinetic energies varied between certain small limits were emitting radiation within a certain frequency limit, with an intensity proportional to the number of molecules. This gives the following expression for the distribution of energy in the black body spectrum:—

$$E_{\lambda}d\lambda = C_1\lambda^{-5}e^{-\frac{C_2}{\lambda T}}d\lambda.$$

Measurements by Lummer and Pringsheim in 1901 showed that this equation was in good agreement with the facts for the shorter wave-lengths, but that it was considerably in error for longer wave-lengths. The equation also indicates that the energy in each wave-length does not increase indefinitely with temperature but approaches a limit. The experiments of Rubens (1865-1922) and Kurlbaum (1901) showed that this was not correct as they obtained intensities in certain wave-lengths greater than the maximum which Wien's equation suggested.

Wien's application of statistical methods to the problem of the equilibrium of radiation between æther and matter was followed by the work of Rayleigh (1842-1919) and of Jeans (b. 1877). They considered the æther itself, and by assigning degrees of freedom to it and applying the principle of the equipartition of energy to these degrees of freedom, deduced an expression for the distribution of energy in the complete spectrum. We have seen (p. 154) that in the kinetic theory of gases, for the case of a perfect gas $p v = RT = \frac{1}{3} M u^2$ where M is the mass of the gas occupying a volume v and u^2 is the mean square of the molecular velocities. $\frac{1}{3} M u^2$, however, is two-thirds of the kinetic energy of the molecules, so that the whole kinetic energy must be equal to $\frac{3}{2} . RT$, or expressed in terms of a single molecule, $\frac{3}{2} kT$ is the average kinetic energy of translation of a molecule, where k is the gas constant for a single molecule. This translatory motion involves three degrees of freedom, so that by the equipartition principle each degree of freedom has associated with it an amount $\frac{1}{2} kT$ of kinetic energy on the average.

On the supposition that the æther has a perfectly continuous structure, i.e. the æther has an infinite number of degrees of freedom, it is evident that in the equilibrium of

æther and matter the æther will have all the energy and the matter none, just as, borrowing an analogy from Jeans, in the case of corks floating on water any energy communicated to the corks finally passes to the water, which has an infinite number of degrees of freedom compared with the cork system.

If, on the other hand, the æther is not continuous, then the number of degrees of freedom will be finite and it becomes possible to deduce the equilibrium conditions. As a result of considering the possible number of types of stationary waves which can persist in an enclosed volume of æther, and which must satisfy certain boundary conditions, Jeans obtained the relation

$$E_{\lambda}d\lambda = 8\pi kT\lambda^{-4} d\lambda.$$

Thus the energy should be distributed so that most of it is in the shorter wave-lengths. Experiment shows that the energy in the very short wave-lengths and the very long wave-lengths is vanishingly small, with a maximum in the infra-red at ordinary temperatures. The Rayleigh-Jeans expression gives no indication at all of such a maximum.

Jeans suggested, however, that the above formula may represent the distribution of energy in equilibrium, but that it may take an infinite time for it to be established, but the excellent agreement of the experimentally determined spectral distributions from different kinds of "black" bodies, does not appear to support this view. It should be pointed out that this expression indicates that the energy in any wave-length should vary as the absolute temperature, and that the experiments of Rubens on the very long infra-red rays reflected from sylvine—the so-called "*Reststrahlen*"—show that in this case the relationship holds good, suggesting that there is an approximation to the truth in the expression, and that the energy is equally divided among all degrees of freedom at low frequencies.

So far no expression based on accepted dynamical principles has been derived to express the energy distribution in complete or full radiation. It may be that the calculation of the number of degrees of freedom is at fault, or that the principle of equipartition does not apply to vibratory motion in the æther. The second of these alternatives has been suggested by Planck (b. 1858), and as a result he

has obtained an expression which gives excellent agreement in every way with the results of experiment. We shall, however, leave the consideration of this work and of the revolutionary concepts introduced into physics as a result to a later chapter.

In our consideration of the problem of radiation we have seen that progress has so far resulted in the deduction of relationships between its quality and quantity and the temperature of the source producing it, without indicating in any way its mode of production. It was, however, known to be vibratory in character, while the presence of emission and absorption lines in spectra suggested that definite free periods existed in the radiation-producing mechanism of matter. The spectrum of full or black-body radiation, as we have seen, consists of radiation of all frequencies the distribution of which seems absolutely determined by its temperature, so that it appeared natural to regard radiation as due in some way to the thermal agitation of the molecules or atoms of the hot body forming its origin.

Thermal agitation, however, is a phenomenon of material bodies, whilst radiation is a phenomenon of the æther, and the problem was to discover the method by which these two manifestations of energy were convertible one to the other. In the case of full radiation corresponding to any given temperature, the work of Gouy (1854-1926), Rayleigh (1842-1919) and Schuster (b. 1851) proved that the infinite number of frequencies existing in its spectrum need have no actual existence in the radiation itself, as they showed that the instruments by which we examine the quality of radiation—spectroscopes and gratings—act as mechanical Fourier analysers, and that in consequence any æthereal disturbance would be analysed into an infinite number of homogeneous vibrations of a simple harmonic type. Hence about 1885 arose the pulse theory of white light, or full radiation.

On this theory radiation was regarded as the effect of the large number of disturbances produced by the mutual collisions and encounters of the charged portions of matter which the evidence of electrolysis indicated might conceivably be capable, even in solid bodies of producing electro-magnetic effects by their motion. Since Maxwell's work on the kinetic theory of gases had shown that the

energies of translation of the molecules of a gas at any temperature varied within very wide limits according to a probability law, it followed that the pulses would vary considerably in character with the nature of the collisions and also with the energies of the particles concerned in them, so that the distribution of energy in the spectrum of full radiation was regarded as the statistical effect of the analysis of many varieties of pulses. It has since been possible to deduce the form of pulses which when analysed into their Fourier components would give a distribution of energy among these components in accordance with Wien's or Planck's laws of energy distribution.

Later work has resulted in the discovery of the electron and its connection with X-rays and other phenomena, and we shall see in a later chapter how J. J. Thomson developed the pulse theory of their production from the electrons of the cathode ray tube as a result of their sudden stoppage or deceleration by collision with the atoms of matter. The facts of the conduction of electricity and of the emission of electrons by hot solids show that they exist in a more or less free state in solids, so that they are now regarded in addition to the charged atoms themselves, as being responsible by their collisions, for the radiation from hot bodies, the encounters of electrons and atoms resulting in the visible and ultra-violet radiations, whilst those of atoms and molecules or the rotations of molecules produce the infra-red radiations.

The problem of accounting for the line spectra of the elements proved extremely difficult. Their constancy of position in spectra under varying physical modes of excitement naturally led to the supposition that they were due to vibrations of definite dynamical systems, presumably the atoms. But serious difficulties very early presented themselves to this supposition. Since each spectral line was considered to represent a separate vibration of the atom, each vibration should, according to the equipartition theory, possess an amount of energy equal to $\frac{1}{2} RT$ per atom, so that an atom capable of giving a spectrum consisting of n lines should possess an amount of vibrational energy of amount $n/2RT$, but the total energy of an atom of mercury from considerations of its specific heat appeared to be only $\frac{3}{2} \cdot RT$ per atom, and for a molecule of hydrogen $\frac{5}{2} \cdot RT$.

This difficulty was fully appreciated by Maxwell, and has been referred to in Chapter VIII.

As spectroscopic facilities improved, however, efforts were made to discover if any relationships existed between the frequencies of the lines in the various spectra. Thus in 1871 Johnstone Stoney (1826-1911) showed that the frequencies of three of the four hydrogen lines were in the ratio of 20, 27 and 32, and in certain other spectra similar "harmonic" ratios were discovered, but it later appeared that relationships of this type were of no more frequent occurrence than would be given by the laws of probability on the assumption of a random distribution of lines in spectra. Huggins (1824-1910) in 1880 discovered the existence of lines in the ultra-violet spectrum of hydrogen, and it was noticed that the wave-length difference between successive lines diminished as the wave-length diminished, suggesting the association of the lines in a series. Somewhat later, Hartley (1846-1913) discovered in the spectra of certain substances in which the lines were associated as doublets, that the difference in frequency of the components of the doublets was constant, while about the same time Liveing (1827-1924) and Dewar (1842-1923) established the existence of series of lines in the spectra of the alkali and the alkaline earth metals.

The most important discovery about this period was that of Balmer (1825-1898) in 1885, who showed that the four lines in the visible spectrum of hydrogen could be represented by the formula

$$\nu = N \left(\frac{1}{2^2} - \frac{1}{m^2} \right)$$

in which m had successively the values of 3, 4, 5, and 6. This formula received confirmation from the fact that the lines discovered by Huggins in the ultra-violet fitted in with this formula, and later that 31 lines seen in the spectra of certain nebulae and also of the solar corona at a total eclipse could be accurately represented by it, so that the whole of these lines were attributed to hydrogen on this account.

For higher values of m the values of ν deduced from this formula approach nearer and nearer to a limiting value which is given by $m = \infty$ and which is termed the root of

the series. Attention was then directed by many workers to the deduction of series for other elements. Among these the most important are Kayser (b. 1853) and Runge (b. 1856), Rydberg (1854-1919), Ritz (1878-1909) and Hicks (b. 1850). As a result of their investigations various formulæ were proposed to represent the frequencies of the members of the series. Rydberg showed that in a great many cases the spectrum of an element consisted of three, or even four series, each of which could be represented by a formula somewhat similar to that given by Balmer, while in many cases the individual members were found to be doublets or triplets. In all cases it was found that the members of a series were separated by larger frequency differences in the lower frequency portions of the spectrum than in the higher, and that they crowded together to a head or root in the higher frequency portion. These series have been designated as Principal Series, first subordinate series and second subordinate series, the subordinate series having their roots or heads in common at some point of the principal series.

Rydberg devoted a large amount of work to the study of these series, and was led to the discovery of some very important relationships between the various series spectra of the same element. The most important of these which was, however, established independently by Schuster shortly afterwards, and is known as the Rydberg-Schuster law, is to the effect that the frequency of the common root of the two subordinate series is given by the difference between the frequency of the root of the principal series and that of its lowest frequency member, that is, by the difference in frequency of the highest and lowest frequency members of the principal series. His formula for a series spectrum is of the form

$$\nu = N \left(\frac{1}{a^2} - \frac{1}{(b + m)^2} \right)$$

in which a and b are constants and N is a universal constant the same for all elements, and known as Rydberg's constant. The existence of this constant excited a great interest, as it indicated the existence of some universal property possessed by all atoms. Physicists were, however, totally unable to suggest what this universal property could

be, and it is only very recently that any interpretation of it has been obtained. We shall see in Chapter XIV how Bohr, by an application of the quantum theory, has given an explanation of both these discoveries of Rydberg.

The next great step in our knowledge of radiation occurred in 1896, when Zeeman (b. 1865) examined the effect of a magnetic field on spectral lines. Faraday's discovery in 1845 of the rotation of the plane of polarisation of a beam of light by a longitudinal magnetic field, and the discovery by Kerr (1824-1907) in 1877 of the change in polarisation of a beam of light by reflection from a magnetic pole, were up to this time the sole evidences of the intimate connection between optical and magnetic effects which Maxwell's theory would lead one to expect.

Shortly before 1896 Lorentz (b. 1853) had been developing an "electron" theory based on Maxwell's theory, which as it made light an electromagnetic phenomenon, suggested that the emission of radiations of definite frequencies from bodies should be the result of the motion, presumably vibratory, of electric charges in the atoms. On this hypothesis, it was naturally expected that a magnetic field would alter the periods of the lines seen in spectra. Attempts had been made previous to 1896 to detect such effects, but had failed on account of the high resolving power required to detect such changes. However, in this year Zeeman observed a distinct broadening in the D lines of sodium when the source was placed under the influence of the magnetic field of a very powerful electromagnet. In a paper *On the Influence of Magnetism on the Nature of the Light emitted by a Substance* describing these results, he writes: "A real explanation of the magnetic change of the period seemed to me to follow from Prof. Lorentz's theory. In this theory it is assumed that in all bodies small electrically charged particles with a definite mass are present, that all electric phenomena are dependent upon the configuration and motion of these 'electrons,' and that light vibrations are vibrations of these electrons. Then the charge, configuration, and motion of these electrons completely determines the state of the æther. These electrons moving in a magnetic field, experience forces which must explain the variation of the period. Prof. Lorentz, to whom I communicated these considerations, at once

kindly informed me of the manner in which, according to his theory, the motion of an electron in a magnetic field is to be calculated, and pointed out to me that, if the explanation following from his theory be true, the edges of the lines of the spectrum ought to be circularly polarised. The amount of widening might then be used to determine the ratio between charge and mass, to be attributed in this theory to a particle emitting the vibrations of light.

“The above mentioned extremely remarkable conclusion of Prof. Lorentz relating to the state of polarisation in the magnetically widened lines I have found to be fully confirmed by experiment.”

Later, by using greater resolving power, Zeeman was enabled to observe the actual splitting up of a line into a number of components as a result of the application of the magnetic field. The effects in many cases were very complicated, and up to the present have not been completely accounted for. The normal Zeeman effect, as the simplest magnetic resolution is called, and which is exemplified in the case of the blue-green cadmium line, shows that under the influence of a magnetic field it splits up into two symmetrically placed with respect to the undisturbed line when viewed parallel to the magnetic field, while when viewed across the magnetic field three evenly spaced lines are seen, one of which coincides with the original line.

The elementary theory of this was simply explained by Lorentz, as any vibration of an electron can be resolved into three mutually perpendicular vibrations of the same frequency, one parallel and two at right angles to the magnetic field. Each of the latter can be further regarded as compounded of circular motions in opposite directions round an axis parallel to the field. The first of these would not be affected by the application of the field, whilst the two circular motions would have their frequencies lengthened and shortened respectively, and hence the effects when a line was viewed either across or along the magnetic lines could be accounted for.

The measurement of the separation then led to the determination of the value of e/m for these particles, whilst the direction of rotation in the circularly polarised components indicated that the particles were negatively charged. The

first values obtained for e/m were of the order 10^{-7} e.m. units, but the most recent determinations have shown that it is 1.77×10^{-7} e.m. units, a value coinciding very closely with the corresponding value for the negative electron as determined by experiments on cathode rays, and the photoelectric effect.

The majority of lines, however, exhibit a type of resolution which is very complicated, as in some cases the number of components in a magnetically-resolved line is as many as six, for instance, in the D_2 line of sodium, whilst the value of e/m deduced from these resolutions has been different, though of the same order of magnitude as that of the negative electron. This discrepancy has, however, been regarded as a result of the incompleteness of the theory which has not yet succeeded in satisfactorily accounting for all the observed effects, though here again Bohr's recent application of the quantum theory has met with considerable success.

The results of Zeeman's experiments thus indubitably established that the atoms of bodies are complex and that all atoms consist, in part, of negatively-charged particles, the motions of which are responsible for the lines in spectra. The identity of the value of e/m obtained for these particles in the normal Zeeman effect with the value obtained for the corpuscle isolated by Thomson in 1897 after Zeeman's discovery, led to the conclusion of the identity of the particles which thus appeared to be a fundamental unit in the structure of matter, and gave confirmation to the electronic theory which Lorentz and Larmor had been developing about this time.

The problem of line spectra was not by any means solved, however. Certain it was that the motions, vibratory or rotational, of the electrons were in some way responsible, but it was exceedingly difficult to imagine the way in which the lines were produced. Their very existence in a spectrum, too, seemed incapable of explanation, for Larmor (b. 1857) had shown that an electron subject to an acceleration must radiate energy and that in consequence its frequency should diminish so that the spectrum of the radiation from a large number of hydrogen atoms should exhibit all frequencies, that is a continuous spectrum, and not sharp lines as it certainly does.

The nature of this difficulty is indicated in the following quotation from a paper by Lord Rayleigh in 1906: "In recent years theories of atomic structure have found favour, in which the electrons are regarded as describing orbits, probably with great rapidity. If the electrons are sufficiently numerous there may be an approach to steady motion. In case of disturbance oscillations about this steady motion may ensue, and these oscillations are regarded as the origin of luminous waves of the same frequency. But, in view of the discrete character of electrons, such a motion can never be fully steady, and the system must tend to radiate even when undisturbed. . . .

"An apparently formidable difficulty . . . stands in the way of all theories of this character. How can the atom have the definiteness which the spectroscope demands? It would seem that variations must exist in (say) hydrogen atoms which must be fatal to the sharpness of the observed radiation; and, indeed, the gradual change of an atom is directly contemplated in view of the phenomena of radio-activity."

Since 1906 this "formidable difficulty" has been largely dispelled, though at the cost of our appreciation of a more fundamental one, and the recognition of the insufficiency of Newtonian mechanics, while variations in the atoms of hydrogen which Rayleigh foreshadowed have, in fact, been postulated, which permit the deduction not only of the existence of sharp lines but their positions and even their intimate structure.

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CHAPTER XI

THE ATOMIC THEORY OF ELECTRICITY

THE electromagnetic theory of Maxwell (1831-1879) and the subsequent verification of its main features by Hertz (1857-1894), as we have seen in a previous chapter, led to the realisation of the importance of the æther in physical and particularly in electromagnetic phenomena. As a result, there followed a period which has been described as the "æther period" in the development of physical science, in which it was considered that all phenomena might possibly be due to variations of stresses and strains in the æther, and that electricity and even matter itself might be capable of resolution into some kinds of local complication of the æther. Maxwell's theory itself, made no effort to arrive at any fundamental notion with regard to the ultimate nature of electricity which, however, seemed to have the characteristics of a continuous, incompressible fluid. There were, however, many facts of experience which seemed to be completely at variance with this idea. It is with these facts and their ultimate development into the atomic theory of electricity or the modern electron theory, that we propose to deal in this and the succeeding chapter.

The origin of the atomic or discontinuous theory of electricity is to be found in the work of Faraday (1791-1867) as far back as 1833, in his investigation of electrolysis. The decomposing action of the electric current had been known for some time previous to this date, but it is to Faraday that we owe the measurement and quantitative examination of the effects here exhibited. Faraday seems to have inherited Davy's ideas as to the ultimate identity of the forces of chemical and electrical action, suggested

no doubt by the association of the two in the voltaic batteries, which were the only sources of "electricity in motion" at that time.

His first step was to investigate the electrolysis of dilute sulphuric acid under varying conditions, such as varying size of electrodes, magnitude of current, and strength of acid. The method he used was to take several vessels containing different strengths of acid, and pass the same quantity of electricity through all of them in series, using different electrodes in each vessel. As a result he deduced that "the chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes," for his experiments showed that the quantity of gas evolved depended only on the quantity of electricity which passed through the circuit. In this connection he remarked in addition, that "the products of the decomposition may be collected with such accuracy as to afford a very excellent and valuable measurer of the electricity concerned in their evolution."

Further researches took the form of investigating the relative weights of the various elements liberated in electrolysis by the same quantity of electricity. In these cases "the chemical action of electricity proved to be perfectly definite" as the quantity of electricity which liberated 1 gram of hydrogen from water also liberated the equivalent weight in grams of any other element from an appropriate solution. These laws suggested that a definite amount of electricity was associated with a definite quantity of matter. Thus, with the atomic weight in grams of a univalent element was associated a certain quantity of electricity, twice the quantity with a bivalent element, and three times the quantity with a trivalent element.

Clausius (1822-1888), in 1857, gave a physical explanation of the mechanism of electrolysis, and suggested that in solutions, the compound molecules under the influence of their thermal motions and collisions became split up into their component molecules or radicles, each of which was electrically charged—the metals and hydrogen being positively charged, and the non-metals and acid radicles being negatively charged. Recombination and re-decomposition would continually occur, but always there would be in existence a number of free positively and negatively

charged "ions" as they were called. Under the influence of an electro-motive force the ions would move in opposite directions to the electrodes, and there give up their charges and be liberated as elements, or set up secondary actions depending on the nature of the ion and the electrodes. Experiments made by Hittorf (1824-1914) in 1853 and by Kohlrausch (1840-1910) in 1879 enabled the velocities of the ions to be determined.

Maxwell experienced difficulty in accepting the implications of Faraday's experiments, but could not in any way explain them. In the chapter on electrolysis in his *Treatise on Electricity and Magnetism* (1873) he writes: "Supposing we leap over this difficulty by simply asserting the fact of the constant value of the molecular charge, and that we call this constant molecular charge, for convenience in description, *one molecule of electricity*." A few lines later he adds that "it is extremely improbable that when we come to understand the true nature of electrolysis we shall retain in any form the theory of molecular charges."

Johnstone Stoney (1826-1911) in 1874 presented a paper on *The Physical Units of Nature* to the British Association, in which the atomic nature of electricity was definitely asserted, and he even calculated the value of the elementary charge from the amount of electricity (9650 coulombs) necessary to liberate 1 gram of hydrogen, which the results of the kinetic theory of gases indicated contained about 10×10^{23} atoms. The result, which was only very approximate, made the unit charge equal to 0.3×10^{-10} electrostatic units. He also introduced the term "electron" to denote the definite elementary quantity of electricity involved in electrolysis.

He was followed in these ideas by von Helmholtz, who in his Faraday lecture to the Royal Institution in 1881 expressed himself in the following manner: "Now the most startling result of Faraday's law is perhaps this, if we accept the hypothesis that the elementary substances are composed of atoms we cannot avoid concluding that electricity also, positive as well as negative, is divided into definite elementary portions which behave like atoms of electricity."

It was about this time that the phenomena accompanying the discharge of electricity through gases were being

studied. In normal circumstances gases are extremely good insulators. If, however, a glass vessel be partially exhausted, it becomes possible to pass a current through it and extremely beautiful coloured appearances are produced in the conducting gas. These effects were investigated in much detail by various workers among whom Faraday, Plücker (1801-1868), Hittorf, Geissler (1814-1879) and Crookes (1832-1919) were most prominent. At moderately low pressures the gas in an evacuated glass tube with electrodes at each end, placed under the influence of the high tension discharge from the secondary of an induction coil, becomes brilliantly luminous, with dark spaces in certain positions, known as the Faraday dark space and the Crookes dark space. Under favourable conditions the luminosity breaks up into a series of beautiful striations. The development of methods of producing higher vacua, by Geissler and others, led to further discoveries as the pressure was lowered. It was found that below a certain pressure the luminosity of the gas disappeared altogether owing to the growth of the dark spaces, and that it gave place to a coloured fluorescence on the sides of the glass containing vessel. Hittorf in 1869 discovered that in such a tube, objects placed between the electrodes cast shadows on the ends of the tubes opposite to the cathode, indicating that radiation of some kind proceeded in straight lines from the cathode. Crookes commenced his investigation on these phenomena about 1870, and showed that a light mica vane mounted on rails between the electrodes, was rotated in such a direction as would be expected if it were bombarded by particles projected from the cathode. It was further discovered that under the influence of magnetic fields, the fluorescent spot opposite the cathode moved in directions which were reconcilable with the hypothesis that negatively charged particles passed from the cathode in the direction of the anode. These strange appearances excited a considerable amount of discussion, two views being advanced as to their nature. One of these was to the effect that the cathode was the origin of a radiation of an undulatory type having a wave-length very different from that of ordinary light. This view was maintained by the German physicists, among whom Goldstein (b. 1850) and Hertz (1857-1894) were conspicuous. In England,

however, largely as a result of the convincing experiments of Crookes, the idea was held that an actual flight of material particles from the cathode occurred in such conditions.

Crookes in 1874 made a happy guess at the nature of the particles, and suggested that they consisted of matter in a new state—"radiant matter," and that the charged particles constituted "the borderland where energy and matter seem to merge." In discussing this radiant matter he writes: "I believe that the greatest scientific problems will find their solution in this borderland, and even beyond it; it seems to me that here we have reached the ultimate realities." Maxwell, it is interesting to note, was inclined to adopt the material hypothesis in the interpretation of these phenomena.

Great difficulty was experienced in accounting in any way for the electrical conductivity of the gas in these circumstances. It was suggested that the gas molecules acquired a charge by contact from the electrodes, and then moved under the influence of the electric force existing between them. This idea, however, did not fit in very well with the observed fact that a definite electro-motive force was required to produce any conduction at all, contrary to the conduction in liquids which occurs under the smallest electric intensity. The first to suggest that conduction in gases was similar to that in liquids was Giese (b. 1847) in 1882, who had been studying the conductivity of flames. His view was that when the electro-motive force exceeded a certain value, a number of the gas molecules broke up into two portions, charged respectively, positively and negatively, but the difficulty remained of ascribing a reason for the opposite charges of the atoms into which it was presumed a molecule broke up. Schuster (b. 1851) in the Bakerian Lecture for 1884 independently suggested the same theory, and supported it by the evidence of mercury which was monatomic, though here of course there was the further difficulty of accounting for the splitting up of the atom itself into two oppositely charged portions. Schuster alone appears to have followed up the "ionic" hypothesis in England, though several continental investigators performed important researches suggested by it. In the Bakerian Lecture for 1890 he

described experiments made with the object of establishing the constancy of charge of the so-far hypothetical particles. By observing the deflection of the cathode rays under the influence of a known magnetic field he found that the value of e/m for the particles in nitrogen was about 500 times the corresponding value found in electrolysis, from which he concluded that the charge was much greater than that involved in electrolysis, and that it could not have been received by contact with the electrodes.

Further discoveries with the cathode rays were made about this time by Hertz and Lenard (b. 1862), as they showed that the rays were able to penetrate thin sheets of metal without losing their power of producing fluorescence, and that they could even be detected outside the tube by the luminosity they produced in the surrounding air. Hertz further showed that the rays possessed the power of rendering a gas conducting even at ordinary pressures.

A tremendous impetus to the study of these and similar phenomena was given by the remarkable discovery of X-rays made by Roentgen (1845-1923) in 1895. The discovery was one of the type which is called accidental, as he noticed that a screen covered with barium platinocyanide, which happened to be near his apparatus, became fluorescent whenever his cathode ray tube was active, in spite of the fact that the latter was completely enclosed in a cardboard box. Further experiment showed that the radiation could pass in varying degrees through all substances, even if they were quite opaque to ordinary light, and that as a general rule the opacity of substances to these new rays depended on their density. Thus the rays produced shadowgraphs of the bones of the hand on a photographic plate owing to the difference in opacity of the flesh and the bones. Roentgen traced the origin of the rays to the point of impact of the cathode rays on the glass of the tube, and showed that they proceeded thence in straight lines. He was very doubtful as to the nature of the rays as they did not suffer deflection in magnetic fields, nor did they exhibit reflection or refraction in passing from one substance to another. The outstanding difficulty in the elastic solid theory of light had been the absence of a longitudinal vibration, so in view of the peculiar properties of the rays he suggested that they might be longitudinal vibrations of

the æther. His uncertainty as to their nature led him ultimately to call them X-rays.

Roentgen's experiments were immediately repeated in almost every physical laboratory in Europe, and a host of new discoveries were made. In particular, Becquerel (1852-1908) was led to investigate the connection between fluorescence and the emission of X-rays, suggested by the phenomena of the cathode ray tube. The salts of uranium were known to be fluorescent, so he exposed crystals of these salts to sunlight and then placed them on a photographic plate wrapped up in black paper which protected it from any visible light. After an exposure of several hours the outline of the crystals could be detected on development of the plate. A repetition of this experiment without previous exposure of the uranium to sunlight resulted in the same photographic effect on the plate. Becquerel immediately connected this with the emission by the uranium of a radiation of its own, independent of previous exposure to sunlight, and subsequent experiment confirmed this, and showed that the intensity of the radiation exhibited no diminution with time. Considerable interest was created in the scientific world on the publication of these results, and efforts were made to extend the list of substances which possessed this property of "radio-activity." All the compounds of uranium showed it, but thorium was the only other element which appeared to have similar properties.

Numerous investigators at about the same time discovered that the X-rays and the radiations from uranium and thorium possessed the power of making a gas conducting. Attempts had been made previously to determine the mechanism of conduction in gases as has been mentioned above, but very little progress had been made owing to the very limited methods available for producing such conductivity. Coulomb (1736-1806), in 1785, had considered the problem as to whether gases conduct electricity or not, and from his experiments, after allowing for conduction over supports, he concluded that there actually was a slight conductivity possessed by gases. Over a hundred years later the question was re-approached by C. T. R. Wilson (b. 1869) who, in 1900, arrived at the same conclusion. The discovery of the new radiations made it

possible to produce a large artificial conductivity, the study of which has resulted in a vast increase in our knowledge of the nature of the electric current and of the nature of electricity itself.

A feature of the conductivity thus acquired by a gas is that on removal of these agencies the conductivity persists for a time and ultimately becomes very small. A great amount of valuable light was thrown on this temporary conductivity by J. J. Thomson (b. 1857), and others working under his inspiration at the Cavendish Laboratory at Cambridge, between 1895 and 1903. J. J. Thomson and E. Rutherford (b. 1871) found that the conductivity of a gas disappeared if it were drawn through a tube containing glass wool, or between plates maintained at a sufficiently large difference of potential, indicating that the conductivity was due to the presence of charged particles. Rutherford, in 1897, experimented to find if the conductivity of gases obeyed Ohm's Law, and it was found that for small potential differences Ohm's Law did hold, but that increasing the potential further produced smaller and smaller increments of current until a potential was reached beyond which no further increase of current took place, the current then being entirely independent of the voltage. The maximum value of the current was called the saturation current from the analogy between the current-voltage curves in this case, and the current-induction curves in the case of the magnetisation of iron. These phenomena received complete explanation on the hypothesis that the rays split up the molecules of the air or other gas into two parts or ions, charged positively and negatively respectively. On the removal of the ionising agency the ions recombine at a rate proportional to the square of the number of ions present, as was confirmed by Rutherford, while the saturation current is obviously due to the action of the potential difference in sweeping the ions to the electrodes as fast as they are formed, before any recombination or diffusion can take place.

Under the same inspiration, experiments were made to determine the velocities of these particles under electric forces and their rates of diffusion and recombination in various circumstances, with the object of determining the physical properties of the ions. Prominent in this work

were Rutherford, Zeleny (b. 1872) and Townsend (b. 1868). The last, in addition, carried out experiments having for their object the measurement of the electric charge carried by an ion, which, it was anticipated, was the same as that carried by a univalent ion in electrolysis. It had been known for a long time that the gases evolved in electrolysis were electrically charged, and that the charged gases had the property of condensing water vapour on them and so forming clouds. Townsend allowed the charged gases to form clouds, and by observations on their rates of fall under the action of gravity, he deduced the radius and hence the mass of each water-drop in the clouds, using a relation, established some time previously by Stokes (1819-1903), which connected the rate of fall of particles in a medium with their radius and the viscosity of the medium. This, combined with the determination of the weight of cloud per unit volume of the gas, enabled him to deduce the number of drops and hence the number of ions per unit volume. The measurement of the total charge per unit volume then permitted the charge on each to be deduced. This exceedingly difficult series of experiments gave fairly consistent results, and indicated that the charge on a gaseous ion was about 3×10^{-10} electrostatic units, a value roughly in agreement with the value of the charge on a univalent ion in electrolysis.

It thus appeared that conduction in gases was due to the splitting up of the molecules into two parts in a somewhat similar way to that in electrolysis, with this difference, however, that in gases the atoms themselves were capable of resolution into parts (even the monatomic gases were capable of being ionised), so that the old idea of the indivisibility of atoms disappeared, and physicists were brought to the study of the architecture of the atom itself.

The mobilities (i.e. velocities under unit electric force) and the coefficients of diffusion of the ions were also determined. It appeared that the negative ions moved quicker, as a rule, than the positive ones, and that the rates of diffusion of the ions were considerably less than those of the gases from which they were derived, suggesting that the charged ions became centres of attraction of the neutral molecules, the positive ions being more efficient in this

respect than the negative ones as they were more sluggish in diffusion as well as in mobility.

But we must now return to the problem of the cathode rays, the solution of which was rendered easier in consequence of the increase of knowledge of electric conduction gained by the study of the ions. In 1895 the controversy regarding the nature of the cathode rays was definitely settled by Perrin who, by connecting an electrometer to a metal plate inside the cathode ray tube, showed that the receipt of a negative charge was recorded by the electrometer whenever the rays were deflected by a magnet so that they struck the plate. This was taken as conclusive evidence that the rays consisted of a flight of material particles as it was inconsistent with any of the known properties of wave motions.

Hertz had tried to deflect the cathode rays by means of an electric force but had failed because, as J. J. Thomson pointed out, the ionisation produced by them in the residual gases formed a surrounding volume electrification and so protected them from the electric field. By working at lower pressures, where the ionisation was very small, Thomson was able to deflect them by both magnetic and electric fields, and by using both fields simultaneously so that the deflections were at right angles to each other, he was able to deduce the values of both e/m and v for the rays, where e is the charge on the particles, m their mass, and v their velocity. Wiechert (b. 1861) in Germany simultaneously and quite independently carried out a similar investigation with approximately the same results, but like Schuster and others he did not interpret the results in the same way as did Thomson.

The value of e/m deduced from Thomson's experiments was about 0.77×10^7 in electrostatic measure, while v varied considerably but was of the order of one-tenth that of light. This value of e/m is about 800 times the corresponding value for that of the hydrogen ion in electrolysis. The interpretation of the difference of the results is explicable in a variety of ways, two of which are more probable than any others. These are that e is the same in both cases so that the mass of the cathode ray particles is about one eight-hundredth that of the hydrogen atom, or that the masses are the same and the charge on the cathode

particle eight hundred times that on the electrolytic hydrogen atom. The evidence was not at that time quite conclusive, but Thomson favoured the former hypothesis, and verified it by redetermining the value of e separately by a method more refined than that of Townsend.

The value of e/m was determined for the cathode rays themselves, whilst that of the charge was determined for ions produced by X-rays or other ionising agencies. In 1899 Thomson made further experiments using the negative particles liberated from the surfaces of metals when ultra-violet light falls on them, and found both e/m and e for the same particles with good agreement with his previous evaluations. The conclusion relative to the smallness of the carrier was thus rendered unquestionable, so that in one respect the alchemist's dream of a common constituent of all matter had come true. Thomson gave the name "corpuscle" to these subatomic portions of matter, though later writers have preferred to use Johnstone Stoney's term "electron."

The same value of e/m was obtained whatever the nature of the residual gas in the tubes, and whatever the nature of the electrodes. As expressed by J. J. Thomson: "Thus on this view we have in the cathode rays matter in a new state, a state in which the subdivision of matter is carried very much further than in the ordinary gaseous state: a state in which all matter—that is, matter derived from different sources such as hydrogen, oxygen, etc.—is of one and the same kind; this matter being the substance of which all chemical elements are built up."

The study of the positive rays, discovered in 1886 by Goldstein, who showed that they travelled through a cathode ray tube in the opposite direction from the corpuscles, was carried out by Wien and Thomson. In all cases it appeared that the value of e/m was never greater than 10^4 , which is about the value for the hydrogen ion in electrolysis, so that, if e is the same as for the corpuscles, the mass of the positive ions must always be of the same order as that of the atoms. The value of e/m for these rays—canalstrahlen or positive rays, as they are called, does depend on the nature of the gas through which the discharge passes.

J. J. Thomson summed up the results of his experiments

in these directions in a paper *On the Masses of Ions in Gases at Low Pressures* in the *Philosophical Magazine* for 1899: "I regard the atom," he writes, "as containing a large number of smaller bodies which I will call corpuscles; these corpuscles are equal to each other; the mass of a corpuscle is the mass of the negative ion in a gas at low pressure, i.e. about 3×10^{-28} of a gramme. In the normal atom, this assemblage of corpuscles forms a system which is electrically neutral. Though the individual corpuscles behave like negative ions, yet when they are assembled in a neutral atom the negative effect is balanced by something which causes the space through which the corpuscles are spread to act as if it had a charge of positive electricity equal in amount to the sum of the negative charges on the corpuscles. Electrification of a gas I regard as due to the splitting up of some of the atoms of the gas, resulting in the detachment of a corpuscle from some of the atoms. The detached corpuscles behave like negative ions, each carrying a constant negative charge, which we shall call for brevity the unit charge, while the part of the atom left behind behaves like a positive ion with the unit positive charge, and a mass large compared with that of the negative ion. On this view, electrification essentially involves the splitting up of the atom, a part of the mass of the atom getting free and becoming detached from the original atom."

Shortly after Thomson's isolation of the corpuscles, it was discovered that they can be obtained in many ways, and that their production in cathode ray tubes is one of the most sophisticated. They were found to be given out by metals and other substances when heated to high temperatures, and also when ultra-violet light falls on metals; in the case of the alkali metals, visible light is sufficient to produce the effect. The thermionic electrons and photo-electrons as they have been called, were investigated by O. W. Richardson (b. 1879), H. A. Wilson (b. 1874), A. L. Hughes, Ladenburg (b. 1878) and others, and have been shown to be the same as the corpuscles of Thomson. The question of the mechanism of their production we shall leave for discussion in the next chapter.

Evidence, too, was available by which the electrons could be identified without the necessity of separating them

from their parent atoms. We have seen in an earlier chapter that Lorentz, adopting the electromagnetic theory, had been led to refer light waves to vibrations of charged particles inside the atom, while Hertz' solution of the problem of the oscillating doublet indicated that in order to obtain visible light, its dimensions must be of the same order as those of the atoms. The measurement of the Zeeman effect enabled the magnitude of the ratio e/m of the particles responsible for the radiation to be determined, and it proved to be the same as e/m for the corpuscle, thus providing strong evidence as to the identity of the two.

Meanwhile, we must return to consider the X-rays and the progress which was being made in the elucidation of the phenomena which they presented. In the case of the X-rays no definite evidence either as to their corpuscular or æthereal nature seemed forthcoming, though there seems to have been a consensus of opinion in favour of the latter. Stokes, in 1896, suggested that the origin of the X-rays was to be found in the sudden deceleration of the cathode rays when they met an obstacle. The rays being charged and in motion, carry with them throughout space electric and magnetic fields which involve a flow of energy in the direction of motion. On meeting an obstacle the portions of the fields near the corpuscle are brought to rest with the corpuscle, whilst the inertia of the remote parts tends to carry them on. Stokes attributed the X-rays to a rectifying pulse which would travel out in all directions and bring the æther to equilibrium. He showed that the properties of such pulses would exhibit similarities with those of X-rays. Thus the pulses would be distributed quite irregularly, and consequently not show interference effects. Thomson, in 1898, worked out the theory of the stoppage of the corpuscles in greater detail in terms of the Faraday lines of force. In his *Corpuscular Theory of Matter* (1907) he writes: "Let us take the case when the velocity with which the particle is moving before it is stopped is small compared with the velocity of light; then before the stoppage the lines of force were uniformly distributed and were moving forward with the velocity V . When the corpuscle is stopped, the ends of the lines of force in the corpuscle will be stopped also; but fixing one end will not at once stop the whole of the line of force, for the impulse which stops

the tube travels along the line of force with the velocity of light, and thus takes a finite time to reach the outlying parts of the tube. Hence when a time t has elapsed after the stoppage, it is only those parts of the lines of force which are inside a sphere whose radius is ct which have been stopped. The lines of force outside this sphere will be in the same position as if the corpuscle had not been stopped. . . . and will pass through the point which the corpuscle would have reached at the time t if it had not been stopped. Since the line of force remains intact it must bend at the surface of the sphere," and so produce an electric force tangential to the sphere. The movement of the electric force then produces a magnetic force at right angles to the electric force and the direction of motion. "Thus the stoppage of the corpuscle causes a thin shell of intense electric (and magnetic) forces to travel outwards with the velocity of light." The thickness of the pulse determines a quantity which we may call the wave-length, and it is to the variation in this quantity that the different degrees of "hardness," or penetrating power of the X-rays are attributed.

Further evidence in favour of the æthereal nature of X-rays was obtained shortly afterwards by Barkla (b. 1877), in 1903, who studied the effects produced by X-rays in passing through matter. It was found that if a metallic plate were placed in the path of a beam of X-rays, corpuscles were ejected from the surface of the metal, and that a secondary X-ray radiation was set up in all directions. A striking feature of this secondary radiation was that its intensity as measured by its power of producing ionisation was greater in certain planes than in others, and that the maximum difference, amounting to about 20 per cent., occurred in two planes at right angles to each other. This effect was strikingly suggestive of the polarisation of the X-rays, and, in fact, until 1912 it remained the most positive direct proof of the electromagnetic nature of the rays. The emission of corpuscles by metals under the action of X-rays was recognised as being similar to the emission of photo-electrons by means of ultra-violet light, so that it seemed probable that the ionisation of gases by these rays was a secondary effect due to the ionising powers of the ejected corpuscle.

CHAPTER XII

THE ATOMIC THEORY OF ELECTRICITY (*Continued*)

MEANWHILE some very startling developments had arisen from the discovery of the radio-activity of uranium. In investigating a number of samples of uranium, Mme Curie (b. 1867) in 1898 discovered that certain naturally occurring varieties had an activity several times what her previous experiments had led her to expect. The most plausible and at the same time most stimulating explanation seemed to be that the abnormal activity was due to the presence of an unknown body possessing more activity than did uranium. In collaboration with her husband she undertook the task of making systematic chemical analyses. The Austrian Government generously provided about a ton of uranium residues from Bohemia. It was found that the activity of the uranium became normal after the bismuth and barium associated with it were removed. By dint of tremendous patience and by working with large quantities of material, a very active preparation of bismuth was obtained. Mme Curie named the impurity mixed with the bismuth, polonium. The polonium was responsible for the activity, for bismuth is not radioactive. The active substance associated with barium was named radium. The radium was separated from the barium by the long and tedious process of fractional crystallisation, as the two substances are extremely alike in their chemical properties. From about one ton of the ores the Curies obtained somewhere in the neighbourhood of a fifth of a gramme of radium. The activity of the new substance was found to be extremely large—about two million times that of an equal weight of uranium. Further investigation showed that it was a new element, and that its atomic weight was about 228, while it filled a gap

in the periodic table which correctly associated it with barium.

All these substances were found to emit radiations which could affect a photographic plate and also ionise gases. In great concentrations they appeared self-luminous and produced luminosity in barium platinocyanide, zinc sulphide and other crystals exposed to their radiation.

Giesel (1852) in 1899 following up an observation of Elster (1854-1920) and Geitel (1855-1923) that a magnetic field altered the ionisation produced by these substances, discovered that they emitted rays which could be deflected by magnetic fields, and that these rays had properties similar to those of the cathode rays.

In 1899 Rutherford discovered that the radiation from uranium was complex, and that one portion of it could not pass through more than about a fiftieth of a millimetre of aluminium foil, while the other could still produce its characteristic effects through several millimetres. The first kind he named α -rays, and the second β -rays, the former being responsible for most of the ionising action and the latter the photographic action.

At a later date Villard (b. 1860) discovered a still more penetrating type of radiation which could pass through several centimetres of lead and still produce a photographic effect. This was named γ -radiation. The properties of these rays then received considerable attention, and efforts were made to elucidate their nature. Becquerel showed that the moderately penetrating particles were easily capable of deflection in a magnetic field and that they behaved in all respects like high velocity cathode rays. It was difficult to determine the nature of the α -rays as no effect of a magnetic field was observable at first. It was suggested that they consisted of an easily absorbed type of X-rays, but this view was rendered untenable by the experiments of Mme Curie in 1900, who found that the absorption of α -rays by matter increased with the thickness of matter previously passed through in marked opposition to the absorption of X-rays. She suggested in explanation that they were projected particles which lost energy in traversing matter: while Strutt in 1901 suggested that they were positively charged particles similar to the positive rays. Rutherford in 1903

succeeded in deflecting the rays with a magnetic field, and found the value of e/m and v for the rays. The values he obtained were $v = 2.5 \times 10^9$ cm. per second, and $e/m = 6 \times 10^3$ e.m. units, indicating that the particles were of atomic dimensions, carrying a positive charge, and on the assumption that the charge was the same as that on a univalent ion, of mass about twice that of the hydrogen atom.

The γ -rays were early shown to exhibit marked resemblances to X-rays. Rutherford, and also McClelland, in 1902 measured the absorption of the rays, and it was found that the absorption was not exponential until the rays had passed through several centimetres of lead, while the failure of all efforts to deflect the rays with electric or magnetic fields was in agreement with the idea of their similarity in nature to X-rays. It was also noticed that γ -rays were only emitted by those substances which also gave out β -rays, so that it appeared that the connection between the β - and γ -rays was the same as that between the cathode rays and X-rays. The γ -rays were much more penetrating than the X-rays.

In 1900 Rutherford made another discovery of great importance in the study of the radioactive substances. The amount of ionisation due to thorium was known to be very much affected by air currents passing over it. He traced this to the emission by the thorium of what was named an "emanation." This emanation could be passed through glass wool and bubbled through water without losing its property of producing ionisation in gases, so that it appeared that the emanation was a kind of gaseous radioactive body. The experiments also showed that the radioactivity of the emanation was not constant but diminished to half value in about a minute, so that after a few minutes no activity was left. A similar emanation from radium was shortly afterwards discovered, but its rate of loss of radioactive power was very much slower than that of the thorium emanation. Further examination and the measurement of their rates of diffusion indicated that the emanations were gases of high atomic weight, and that they were probably monatomic since they suffered no change when subjected to most violent physical and chemical treatment.

Some very interesting results which shed much light

on the processes of radioactivity were also obtained by Crookes in 1900. He found that by chemical treatment he could separate a constituent from uranium which exhibited all the activity, measured photographically, of the original, whilst the uranium itself had its activity reduced to zero. He named the separated constituent uranium X. Becquerel confirmed this, but showed that the activity of the uranium X after a year was zero, and that the uranium had fully recovered its activity. Rutherford and Soddy in 1902 discovered that a similar separation of activity was possible in the case of thorium, and they named the separated portion thorium X. After a month the activity of the thorium X was found to be zero, whilst the thorium had regained its full activity.

The investigation of the rates of decay and rise of the activities showed that they followed an exponential law. Thus in the case of the thorium X it was found that its activity fell to half its value at any instant in about four days, while in the case of the uranium X the corresponding time was about twenty-two days. This type of change is typical of the mono-molecular kind met with in chemistry, when a molecule dissociates into simpler products. In the present instance since the uranium and thorium are elements, it suggests that the dissociation of the atoms of these substances produces atoms of something else having different radioactive properties. Furthermore, experiments showing that the rates of rise and fall of activity were totally unaltered by the most drastic physical and chemical treatment were strongly suggestive of the atomic origin of the phenomena of radioactivity.

As a result of a detailed study of the activity, Rutherford and Soddy (b. 1877) in 1902 put forward the suggestion that radioactive matter was constantly producing from itself a new kind of matter, in consequence of atomic disintegration. The further disintegration of the new product in conjunction with the association of helium with radioactive minerals suggested that helium was one of the products of the transformation. This was confirmed in 1903 by Ramsay (1852-1916) and Soddy, by their proof of the presence of helium in the gases evolved from water by the action of radium in solution, while Rutherford's measurement of e/m of the α -rays which was reconcilable with the

assumption that they consisted of particles with twice the charge on a univalent ion, and a mass four times that of the hydrogen atom, led to the identification of the α -ray with a positively charged helium atom.

Rutherford and Soddy developed the theory further in a paper entitled *Radioactive Change* in 1903, in which the consequences of the theory were pointed out. The following quotation from Rutherford's *Radioactive Substances and their Radiations* gives a summary of their theory: "The theory supposes that, on an average, a definite small proportion of the atoms of each radioactive substance becomes unstable at a given time. As a result of this instability the atoms break up. In most cases, the disintegration is explosive in violence, and is accompanied by the ejection of an α -particle with great velocity; in a few cases α and β -particles are expelled together, while in others a β -particle alone escapes. In a few cases, the change in the atom appears to be less violent in character, and is not accompanied by the expulsion of either an α or β -particle. The expulsion of an α -particle of atomic weight 4, leaves behind it a new system lighter than the original one, and possessing chemical and physical properties quite different from those of the original element. This new system again becomes unstable, and expels another particle. The process of disintegration once started, proceeds from stage to stage at a definite measurable rate in each case."

That the α -particles carry a charge equal to twice that on the electron was confirmed experimentally by Rutherford and Geiger (*b. r882*) in 1908, while in 1909 Rutherford and Royds obtained definite proof of the identity of the α -particles with helium, by exposing lead to the intense α -particle bombardment from large quantities of radium emanation, for on boiling the lead *in vacuo* and passing an electric discharge through the evolved gases, the spectrum of helium was obtained, whereas lead by itself on such treatment did not enable the helium spectrum to be produced.

It is impossible to do more than indicate very briefly the progress which has occurred since this time. The application of the disintegration hypothesis has been found in every case to give satisfactory results. In an extremely short space of time over thirty radioactive elements have

been discovered. They consist of three series, of which one—the actinium series—is probably connected with the uranium series. Their radioactivity varies to an enormous degree among the different elements—uranium, for instance, disintegrates so slowly that it is calculated about 6×10^9 years are required for one half of it to suffer transformation, while actinium A decays to half value in 0.002 second. In both the uranium and thorium series the evidence points to the end product of the series being lead. Since the lead formed as a result of the disintegration remains *in situ*, the evaluation of the ratios uranium to lead and thorium to lead, combined with the knowledge of the intermediate transformation constants, enables an approximate estimate of the age of various rocks to be made, though the two ratios do not give quite consistent results. The values obtained are of the order 500,000,000 years.

The study of the passage of these various rays through matter has led to a great increase in our knowledge of the structure of the atom. In the case of the α -rays W. H. Bragg (b. 1862) showed that the α -rays corresponding to any particular radioactive change were characterised by a definite range in air, and hence a definite initial velocity of ejection, so that each type of atomic disintegration must be of a perfectly definite character. The velocities of expulsion were found by Rutherford to vary between 1.4 and 2.2×10^9 cm. per second. In passing through metallic films the α -particles suffer deflections, the magnitude and frequency of which were found to be much greater than that calculated on Thomson's theory that the atom consisted of a sphere of positive electrification in which were embedded negative electrons. To reconcile theory with experiment, Rutherford proposed the nuclear type of atom in which the positive charge and also the greater portion of the mass of the atom are supposed to be concentrated on a central nucleus. Experiments by Rutherford and Geiger showed that the dimensions of the nucleus were smaller than 10^{-12} cm., the radius of the atom, according to the kinetic theory, being about 10^{-8} cm., so that the atom would appear to be a kind of miniature solar system. The value of the central charge deduced from these experiments appeared to be about $\frac{1}{2}Ne$ where N is the atomic weight, and e the unit charge.

The β -particles expelled by radioactive substances are exceedingly complex. They are ejected with extremely large velocities varying from 30 to 99 per cent. of the velocity of light, and in many cases consist of homogeneous groups. There is considerable evidence that the β -particles originate in the nucleus of the atom, which would thus appear to be a very complicated unit. The β -particles in their passage through matter are subject to scattering so that they soon lose their original direction of motion. The occurrence of β - and γ -rays in the same radioactive change suggests a close connection between the two, though up to the present there is a great deal which is obscure in their relationship.

Meanwhile, experiments showing the relationship between cathode rays and X-rays were being carried out by Barkla, Whiddington and others. We have seen in the last chapter that Barkla in studying the effect of the scattering of X-rays had demonstrated the production of secondary X-rays when these strike matter. Further experiments in 1906 and 1907 showed that the scattered radiation from metals of atomic weight less than 40 was of the same kind as the primary radiation exciting it. For metals of atomic weight greater than 40, it was found that radiations characteristic of the metal, but totally independent of the intensity of the primary radiation could be produced. These characteristic radiations were recognised by their absorption coefficients in aluminium, and it appeared that the higher the atomic weight of the element the greater was the penetrating power of its characteristic radiation. Extrapolation from these results made it possible to predict the value of the absorption coefficient in aluminium of the characteristic radiation from uranium. Close agreement was obtained with the observed absorption coefficient for the γ -rays of uranium, thus lending support to the theory of the similarity of X-rays and γ -rays.

Later it was shown that in general two types of characteristic radiation were emitted which were called the K- and L-series—the former being of greater penetrating power than the latter. The conditions under which these radiations were produced were then investigated, and it appeared from the experiments of Barkla and Sadler that in order to excite the radiation characteristic of any metal,

that radiation itself or a "harder" one must be a constituent of the primary radiation producing it, thus suggesting an analogy with Stokes' Law, which at first led to the calling of these radiations fluorescent radiations.

They also studied the emission of high speed electrons by matter under the influence of characteristic X-rays, and showed that the velocity of expulsion of these was constant for a given radiation, independent of its intensity or of the nature of the metal. It is thus determined by the quality of the X-rays, and is greater the greater the atomic weight of the metal whose characteristic radiation is used. Whiddington in 1911 then attacked the same problem from the other end. He measured the velocities of the cathode rays which were just sufficient to excite the characteristic radiation in metals of different atomic weights, and found that they were precisely the same as the velocities of expulsion of the electrons by the characteristic rays which they themselves could produce.

It is in the elucidation of these transformations of energy between the β - radiation and γ - radiation types that we encounter one of the most urgent problems of modern physics. The liberation of slow electrons by ultra-violet light also presents us with the same difficulty. In this case it was shown by Lenard that the velocity of the ejected electrons is independent of the intensity of the incident light, and is solely determined by its wave-length, increasing as the wave-length diminishes as proved by the experiments of Ladenburg.

The following passage by J. J. Thomson from his article on the *Conduction of Electricity in Gases*, in the 11th edition of the *Encyclopædia Britannica*, is both illustrative of the difficulty involved and of the profound alterations which we may find it necessary to make in our conception of the æther and of the nature of radiation. "What is the source of the energy possessed by these corpuscles? Is it in the light, or in the stores of internal energy possessed by the molecule? Let us follow the consequences of supposing that the energy comes from the light. Then, since the energy is independent of the intensity of the light, the electric forces which liberate the corpuscles must also be independent of the intensity. But this cannot be the case if, as is usually assumed in the electromagnetic theory,

the wave front consists of a uniform distribution of electric force without structure, for in this case the electric force is proportional to the square root of the intensity. On the emission theory of light a difficulty of this kind would not arise, for on that theory the energy of a luminiferous particle remains constant as the particle pursues its path through space. Thus, . . . the velocity of emission would not depend on the intensity of the light. There does not seem any reason for believing that the electromagnetic theory is inconsistent with the idea that on this theory, as well as on the emission theory, the energy in the light wave may, instead of being uniformly distributed through space, be concentrated in bundles which occupy only a small fraction of the volume traversed by the light, and that as the light wave travels out the bundles get further apart, the energy in each remaining constant."

On this theory then Thomson attributes a kind of fibrous structure to the æther, or what is practically the same thing, supposes that the Faraday lines of force have an actual material existence, and that light waves consist of the vibrations of these. Some such localisation of the energy in a wave front seems to take place in practice, for the photoelectric effect takes place without delay in cases where the energy falling on an area equal to the cross-section of the atom would not reach the value actually possessed by the ejected electron for years. It seems impossible that an atom can collect energy from a volume very large compared to its own, yet the results might be interpreted that way. Trigger action has been suggested by which it is supposed that at any given instant a certain number of atoms are almost in a condition to expel an electron, but such a theory does not appear to meet the fact that light of a definite frequency is necessary. There are many difficulties in the way of a theory such as that of Sir J. J. Thomson. Not the least of these is the difficulty of explaining interference phenomena in terms of these bundles of energy, or vibrating Faraday tubes, as the case may be.

In the case of the X- and γ -rays, Bragg in 1911 put forward a corpuscular theory of these rays in which he assumed that they were neutral doublets. On his view the γ - and X-rays consisted of a negative electron to which an equal amount of positive electricity was attached. In

their passage through matter a number of the doublets were supposed to lose their positive charge, while the electrons went on with the velocity which characterised the doublets before their disintegration. On this theory the great penetrating power of a γ or an X-ray was due to its neutrality and high velocity.

Shortly after this, however, the long uncertainty as to the nature of these rays was settled in favour of the wave theory. It had long been suspected that the wave-length of these rays, if there were any such quantity, should be very much smaller than that of ordinary light. Now all theories of wave-motion agreed in their prediction of a refractive index which tended to unity as the wave-length diminished, so that the absence of refraction, as was pointed out by Schuster, was not evidence against such a theory. Nor was the absence of diffraction by diffraction gratings, for in order that light may be analysed by a grating the grating space must be of the same order of magnitude as the wave-length of light. So that if X-rays were to be thus analysed it was evident that it would be necessary to use gratings far beyond our capacity to produce mechanically.

In 1911 Laue (b. 1873) conceived the idea of using the regular arrangement of the atoms in crystals as a grating. Whereas ordinary gratings consist of periodic inequalities on a surface, the grating presented by a crystal has the periodic inequalities or atoms distributed in three dimensions, so that it was to be anticipated that any diffraction effects would be extremely complicated. Laue worked out completely the mathematical part of the problem, and showed that if a beam of X-rays traversed a crystal placed some distance in front of a photographic plate, a very marked photographic effect should be produced in the direct path of the beam and that it should be accompanied by a series of other spots due to the diffracted radiation, and that these should be distributed in a regular manner round the central spot.

The idea was put to experimental test early in 1912 by Friedrich and Knipping with immediate success. Beautiful patterns depending on the orientation of the crystal were obtained, which from their regularity confirmed the hypothesis of extreme regularity of structure in crystals. It

was immediately recognised that this phenomena placed in the hands of the physicist a new and extremely potent instrument for the elucidation of the problem of crystal structure, about which little, apart from the external form, was known, and also that given the crystal structure the wave-lengths of the X-rays could be determined.

It was pointed out by W. L. Bragg (b. 1890) who, in conjunction with W. H. Bragg, immediately applied this method that the dark spots on the transmission photographs are found at places corresponding to the reinforcement of waves reflected from successive planes of the crystal which are rich in atoms, so that the effect should be produced by reflections from cleavage planes or natural faces. This was confirmed, and since then the reflection method has superseded the transmission method on account of the greater facility with which it enables the interpretation of the spots to be made.

The first problem, therefore, was to determine the structure of one crystal. This was first done for the cubic type of which rock salt is an example. If it be assumed that in such crystals the atoms are regularly arranged at the corners of cubes, it becomes possible to deduce relations connecting the angles between planes which contain minimum or maximum numbers of atoms. The deductions from this hypothesis were fully confirmed by experiment, so that since the arrangement of the atoms, the density of the crystal and the weights of the sodium and chlorine atoms are known, the distance apart of the atoms in the "space lattice" of rock salt can be deduced. This being known observation of the angle of diffraction enables the wave-length of the X-rays to be deduced. As an example the distance between the planes of atoms parallel to the natural faces of rock salt is 2.81×10^{-8} cm., and the wave-length of the characteristic X-rays of palladium or the X-rays from a tube using palladium as the source of the rays when the velocity of the cathode rays exceeds a certain minimum value, is 0.576×10^{-8} cm., or about 10,000 times less than the wave-length of sodium light.

Using this method it has been shown by numerous investigators that the radiation from an X-ray bulb consists of a general radiation similar to white light accompanied by strong homogeneous radiations depending on the metal

used as the anticathode. Thus Bragg found that a platinum anticathode emitted, together with general radiation, a homogeneous radiation of wave-length 1.10×10^{-8} cm. and that its absorption coefficient in aluminium was the same as that of the L characteristic radiation of platinum as determined several years before by Barkla. That the γ -rays also were of the same nature was shown by Rutherford and Andrade (b. 1887) in 1914.

It thus appears that the single pulse theory of the X-rays does not account for the whole of the phenomena. It may account for the "white X-rays" which are analysed by the crystals into a continuous spectrum in the same way that the pulses constituting "white light" are analysed by prisms, gratings and such like, but the existence of well-marked definite frequencies show that something more is involved, and that the impact of cathode rays sets something very deep-seated in the atom into action.

The determination of the characteristic frequencies of the X-rays from various elements was then undertaken by Moseley (1888-1915) in 1913 with great success. He investigated the elements whose atomic weights were between 27 (aluminium) and 197 (gold). The characteristic frequencies were found to fall into two sets the K- and the L-series, each of which consisted of several lines, the K-series being of much shorter wave-length than the L-series. An extremely important result emerged from the measurement of these frequencies, for Moseley showed that

$$\nu = A(N - b)^2$$

where ν is the frequency of the radiation, N is the number of the element in the periodic table or the atomic number, while A and b are constants for all elements for corresponding members of the K- or L-series. Now in Chapter V we found that in the periodic classification there were certain irregularities which made tellurium come before iodine and argon before potassium, contrary to their known atomic weights. Moseley's experiments, however, showed that though the atomic weights of tellurium and argon were greater than those of iodine and potassium, yet the values of N obtained from this equation confirmed the practice of placing these elements in association with elements resembling them in properties in spite of the

discrepancy regarding the atomic weights. Thus the importance of the position of an element in the periodic table as determining its properties was strikingly emphasised. The question now arose as to what it was in an atom which determined its position in the table. The experiments of Rutherford and Geiger and of Marsden (b. 1888) on the scattering of α -rays had suggested that the atom consisted of a nucleus which was the seat of an intensely concentrated positive charge, neutralised by an equal negative charge distributed over surrounding electrons, and that the magnitude of this charge was not very far from one-half the atomic weight. This idea received strong support from the discovery by Fajans (b. 1887) and Soddy in 1913 that in the expulsion of a doubly-charged α -particle a radioactive element moved to a position two places to the left in the periodic table, while the expulsion of a β -particle caused the element to move one place to the right—the loss of a positive charge putting an element among the more electro-negative ones and *vice versa*.

Radioactive substances are known in which the expulsion of an α -particle is followed by the expulsion of two β -particles, so that on the theory of Soddy and Fajans the element resulting from these changes should occupy the same place in the periodic table as the element before the emission of the α -particle. This results in two elements occupying the same position in the table. Their atomic weights differ in the case under consideration by four units, while the charge on the atom remains the same, the loss of the two β -particles compensating for the loss of the α -particle. Further investigation of the radioactive substances resulted in many more places in the periodic table being occupied by two or more elements differing in atomic weight, but having the same nuclear charge. Elements exhibiting these features were termed “isotopes” by Soddy.

The inference was extremely strong that the chemical and physical properties of an element do not depend so much on the atomic weight as on the magnitude of the atomic charge, which appeared to be identical with the atomic number, as was suggested by van den Broek in 1913. These ideas received striking confirmation from later work which we shall consider in a later chapter.

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CHAPTER XIII

THE THEORY OF RELATIVITY

“THE beauty and clearness of the dynamical theory which asserts light and heat to be two modes of motion is at present obscured by two clouds.” This statement was made by Kelvin towards the end of last century in a discourse at the Royal Institution on *Nineteenth Century Clouds over the Dynamical Theory of Light and Heat*. The clouds he referred to were our difficulties respecting the theorem of the equipartition of energy in the radiation problem, and the apparent non-existence of relative motion of matter and æther in electrodynamics. In the one case the application of classical mechanics led to a deduction of the energy distribution in the spectrum of a black body completely at variance with the results of experiment, while the refusal of the Michelson-Morley experiments to show any motion of the earth through the æther seemed to indicate that the postulation of an æther was unnecessary.

Since then two of the most revolutionary theories that have been discussed since the time of Copernicus have been proposed, and have completely revolutionised our point of view, and necessitated a very critical study of the foundations of mechanics.

The first cloud to which Kelvin referred is one which has been with us in certain aspects for many years and dates back to the time of Newton. In establishing his dynamical principles Newton tacitly assumes that all velocities and motions can be measured with reference to an absolute standard space without committing himself to the possibility of our being able to identify a particular system of axes in space. In the Scholium to the Definitions in his *Principia* he writes: “Time, space, place and motion are

well-known to all. It is to be observed, however, that the vulgar conceive these quantities only in their relationships to sensible objects. . . . Absolute, true, and mathematical time of itself and from its own nature, flows evenly on without respect to anything external. . . . Absolute space from its own nature without respect to anything external remains always the same and immovable."

Thus to Newton there appeared no difficulties regarding the actual nature of space and time, which were conceived as existing independently of each other and of all phenomena, while the idea of simultaneity in time presented no ambiguity.

Now it can be shown that the Newtonian equations of motion retain the same form if the co-ordinates x , y , z and t , are changed from those of an ideal fixed absolute system to those of a system moving with a uniform translatory motion with reference to the fixed system. That is, all systems moving with constant velocity are equally suitable as reference systems for Newtonian dynamics. Since the earth's absolute velocity may be considered to be changing only slowly, it is possible to use a system of axes fixed relatively to the earth for the treatment of terrestrial phenomena, while similarly as regards the solar system the constant absolute velocity of its centre of mass allows us to choose axes passing through it, in dealing with problems of celestial mechanics. In this sense, then, the Newtonian system of dynamics is referred to a fixed reference system.

It was not long, however, before difficulties arose. Bradley (1692-1762) in 1727 made the discovery that the apparent direction of the stars was altered by the earth's motion. This effect was attributed to the relative motion of the light corpuscles and the earth in its orbit. It follows from elementary considerations that the angle of aberration is a function of v/V where v is the velocity of the earth and V that of light, and it was found that observations of the angle of aberration agreed with the theory so that the velocity of light could be determined by such observations. The agreement obtained in this way thus clearly indicated that the light transmitting medium must be at rest with respect to the observer.

The development of the wave theory of light in the

hands of Young, Fresnel and others, in which an æther was postulated, and to which were referred the disturbances of light and later of electromagnetic waves, led to the anticipation that an absolute reference system was available as it seemed probable that the æther was "stagnant" or in absolute rest. Young was of opinion that matter presented an open structure to the æther, which passed through it without interference "like the wind through a grove of trees." Thus, early in the nineteenth century in considering the luminiferous æther, the question of the velocity of the earth relative to this medium was at once discussed.

In 1818 Arago attempted to solve the problem. Since the refractive index of a transparent substance is the ratio of the velocity of the incident light to that of the refracted light, he considered that if a prism were moving through the æther towards a source of light, the velocity of the incident light relative to the prism would be increased, while he thought the velocity in the prism would be unaltered. Arago examined the light from stars in different directions so that the earth would be travelling towards some and receding from others, but he did not succeed in detecting any change of refractive index.

Fresnel pointed out that no change in refractive index would occur if the motion of the prism through the æther resulted in a change of velocity of the light in the prism, relative to the æther, from u to $u + (1 - 1/\mu^2)v$, where u is the velocity in the prism at rest and v is the velocity of the prism when moving. That is to say the moving prism communicates to the light a fraction $(1 - 1/\mu^2)$ of its own velocity. The quantity $(1 - 1/\mu^2)$ is known as Fresnel's convection coefficient.

This result is a consequence of Fresnel's ideas on the constitution of the æther in material bodies. On his theory the different velocities of light in different media are due to the different densities of the æther in media, so that if matter is to move in an æther which outside matter is at rest, some of the æther in the matter must be "convected" or dragged along with it in order to maintain continuity of the medium.

In 1851 Fizeau (1819-1896) carried out experiments with the object of verifying Fresnel's suggestion. He devised

an arrangement in which a ray of light was divided into two parallel beams which were then made to traverse two parallel tubes filled with water. Mirrors suitably placed made each beam traverse the same paths in opposite directions. After passing through the tubes the two beams were brought together again and the interference fringes produced by them were observed. It was found that a shift of the interference fringes was produced on setting the water in a series motion through the two tubes. Fizeau found that the observed shift was in complete accord with what was demanded by Fresnel's brilliant deduction that the velocity of light relative to a material medium, in addition to depending on the nature of the medium, depends also on the velocity of that medium relative to the æther. Up to this time all results of experiments on the optical effects produced by the relative motion of matter and æther were, in accordance with Fresnel's convection hypothesis, combined with that of a fixed or absolute æther outside material bodies.

The question was, however, not regarded as quite settled by the experiments of Fizeau. A strong objection was the fact that the convection coefficient varied with the wavelength of light, and this was considered to be an impossible physical interpretation of Fresnel's hypothesis. Accordingly, in 1881, Michelson (b. 1852) and Morley attempted to observe differences in the velocity of light relative to the earth, when the latter is moving in different directions relative to the sun and presumably to the æther. The method they employed consisted in dividing a beam of light incident at 45° on a half-silvered mirror, into two portions, one of which after reflection travelled at right angles to its original direction to a plane mirror, whence it was reflected back to the half-silvered mirror, whilst the second one after refraction proceeded in its original direction to another plane mirror from which it also was reflected back to the half-silvered mirror. Portions of the two beams reflected and transmitted by this mirror were then examined for interference phenomena. The whole apparatus was mounted on a sandstone slab floated on mercury so that either of the two beams could be made to coincide with the direction of the earth's motion relative to the sun. The point of the experiment was that in con-

sequence of the velocity of the earth through the æther, the retardation of the two interfering beams would depend on the directions of the two beams relatively to the æther, and that a change in their direction would alter the retardation and so cause a shift of the interference bands, which shift it was calculated should be easily measurable. To the surprise of every one it was found that no trace of any displacement could be detected. The experiment was repeated by Morley and Miller, in 1905, with the greatest possible precautions but with the same absence of result.

An explanation of the absence of any shift of the fringes was suggested in 1893 by FitzGerald (1851-1901) and independently in 1895 by H. A. Lorentz (b. 1853). This explanation was to the effect that as a result of the interaction of matter and æther all lengths in the direction of motion through the æther were contracted in the ratio of $(1 - v^2/c^2)^{\frac{1}{2}} : 1$, as compared with their lengths when at right angles to this direction. This apparently wild suggestion was not considered further at the time until Lorentz revived it and indicated a possible reason for the contraction. This he found from the behaviour of the electric and magnetic fields associated with moving charges. J. J. Thomson, in 1881, showed that the electric field due to a uniformly moving charged particle could be obtained from that of the particle at rest by a transformation which is equivalent to considering lengths parallel to the direction of motion diminished in the ratio $(1 - v^2/c^2)^{\frac{1}{2}} : 1$.

"We can understand the possibility of the assumed change of dimensions," writes Lorentz, "if we keep in mind that the form of a solid body depends on the forces between its molecules, and that in all probability, these forces are propagated by the intervening æther in a way more or less resembling that in which electromagnetic actions are transmitted through this medium. From this point of view it is natural to suppose that, just like the electromagnetic forces, the molecular attractions and repulsions are somewhat modified by a translation imparted to the body, and that this may very well result in a change of dimensions." From this point of view the null result of the Michelson-Morley experiment appears to be due to a compensating effect inherent in the constitution of matter, for the magnitude of the contraction does not involve any

of the known properties of matter. In the experiments of Morley and Miller the distances between the mirrors were made to depend on the length of either a metal or a wooden rod, with no difference to the result.

Thus Lorentz' attitude was, that on the assumption of an immovable æther, "Michelson's experiment *proves* the changes in dimensions in question, and that the conclusion is no less legitimate than the inferences concerning the dilatation by heat or the changes in the refractive index that have been drawn in many other cases from the observed position of interference bands." The shrinking being admitted, the problem was now to propose the mechanism by which it is produced in material bodies. This Lorentz did in the development of his theory of electrons which owed its origin to Lorentz and Larmor (b. 1857) even before the recognition of such particles had been experimentally realised.

It was about this time that the results of Sir J. J. Thomson's beautiful experiments leading to the "isolation" of the electron became known. In consequence of this work it was established that the negative electron was a universal constituent of all matter, thus providing the first experimental support to the ideal of the common origin of all matter. The electron was at first studied in the cathode rays of the vacuum tube, and it appeared that the electron was characterised by having a constant value of e/m (see Chapter XI), in which e had the same value as the unit charge on a monovalent ion in electrolysis, m was about $1/1800$ that of a hydrogen atom, while its velocity was a quantity which varied between very wide limits.

In the paper previously referred to J. J. Thomson had shown that a charged sphere had mass in virtue of the charge it possessed. "The charged sphere," he writes, "will produce an electric displacement throughout the field; and as the sphere moves, the magnitude of this displacement at any point will vary. Now, according to Maxwell's theory, a variation in the electric displacement produces the same effect as an electric current; and a field in which electric currents exist is a seat of energy; hence the motion of the charged sphere has developed energy; and consequently the charged sphere must experience a resistance as it moves through the dielectric.

But as the theory of the variation of the electric displacement does not take into account anything corresponding to resistance in conductors, there can be no dissipation of energy through the medium; hence the resistance cannot be analogous to an ordinary frictional resistance, but must correspond to the resistance theoretically experienced by a solid moving through a perfect fluid. In other words, it must be equivalent to an increase in the mass of the charged moving sphere." Thomson further showed that the mass of a charged sphere varied with its velocity, becoming infinite for a velocity equal to that of light.

The discovery of the existence of β -particles from radium, that is, negative electrons with velocities approaching that of light, suggested the testing of these results. Larmor, in 1895, had put forward the idea that the mass of ordinary matter was of the electromagnetic type and on this assumption, together with a suitable hypothesis as to the form of the electron, the variation of the mass of the electron with its velocity was calculable.

Lorentz, in explaining the definite refusal of the Michelson-Morley experiment to indicate the relative motion of the æther and the earth, had, as we have seen, been led to suggest the contraction hypothesis as a compensating effect hiding the phenomenon of the relative motion from observation. The contraction he then suggested was due to the contraction of the individual electrons in their direction of motion, and on this assumption he then calculated the variation of the mass of the "contractile" electron with velocity.

Kaufmann (b. 1871) in 1901 and again in 1906, and Bucherer (b. 1863) in 1909 experimentally determined this variation by using the β -particles from radium. Kaufmann's early experiments seemed to agree better with Abraham's theory of a rigid electron, but his later ones, and those of Bucherer, agreed extremely well with the Lorentz contractile electron. Thus the contraction, the existence of which seemed to be substantiated by these experiments, appeared to be a fundamental property of matter.

Much of the above-mentioned work of Lorentz arose out of his development of the electron theory. On this theory the whole of the universe is supposed to consist only of electricity and æther. Magnetic poles are given no existence,

only magnetic force due to motion of charges, whilst a polarised dielectric is resolved into its component charges. Refraction, dispersion, and absorption of light are accounted for by the motion of the electrons excited by the luminous waves and a consequent reaction on the æther; whilst the emission of light by incandescent solids is due to disturbances of the electrons. On hypotheses such as these he was able to re-establish Maxwell's fundamental equations of the electromagnetic field. These equations, however, only referred to a co-ordinate system at rest relatively to the æther. Lorentz then attempted to deduce the equations of electrodynamic phenomena in a medium which was moving relatively to the observer. As a result he found that the fundamental equations did not retain their simple form if the Newtonian transformation, which experience had shown to be correct in ordinary dynamics, were used. However, by 1903 he showed that if the transformation

$$x' = \beta(x - ut), \quad y' = y, \quad z' = z, \quad t' = \beta(t - ux/c^2)$$

where $\beta = (1 - u^2/c^2)^{-\frac{1}{2}}$ were used instead of

$$x' = x - ut, \quad y' = y, \quad z' = z, \quad t' = t,$$

the equations did keep the same form. In addition to the contraction in the direction of motion, however, it appeared that "time" in the transformed system differed from that in the original system. This time Lorentz called the "local" or "effective" time, while the transformation is usually referred to as the Lorentz transformation.

From this it appears that the relativity principle of Galilei-Newtonian mechanics does not hold in electrodynamics. Still, the fact that a transformation had been found which left the form of the equations unchanged when the co-ordinate system was changed from one set of axes to another moving with constant velocity relative to it, showed that there was something very fundamental to be explained.

It was at this stage that Einstein (b. 1879) commenced his investigations. His results were published in 1905, and are usually referred to as the Special Theory of Relativity to distinguish it from the General Theory arrived at in

1915. Einstein attacked the problem from quite a different standpoint from that of Lorentz. Lorentz starting from the conception of a motionless æther was led to expect a positive result from the Michelson-Morley experiment. The unexpected negative result then led him to the contraction hypothesis, which was confirmed by the experiments of Bucherer, and later to the Lorentz transformation which satisfied the relativity principle, and from which can be deduced the experimental fact that light travels with the same velocity c with respect to *both* systems of co-ordinates, viz. x, y, z, t and x', y', z', t' .

Einstein, on the contrary, commenced by postulating the principle of relativity, and by fully accepting the Michelson-Morley experiment that we can observe no difference in the velocity of light as a result of our motion through space. By a masterly analysis of the physical significance of time and space, and of the implications of the Newtonian dynamics, he showed that "length" was not an inherent property of matter and had no meaning unless the motion of the observer was specified, while similarly "time" also had no meaning apart from an observer. Einstein also showed that the variation of mass with velocity which had been calculated by Lorentz for a contractile electron was a general property of matter and not only of charged particles.

He then deduced the same transformation equations as those previously obtained by Lorentz, and showed that the "local" or "effective" time on the moving system is really the true time, since an observer on the system could not detect his own motion by measurements on the velocity of light. These transformation equations reduce to the Newtonian form if u is made very small compared with c , so that the same transformation holds in all dynamical systems, the Newtonian transformation being merely a particular case of Einstein's depending on the assumed absolute character of time and space and the smallness of the velocities considered.

As regards the Fitzgerald-Lorentz contraction it appears, that, quoting Eddington, "When a rod is started from rest into uniform motion, nothing whatever happens to the rod. We say that it contracts; but length is not a property of the rod; it is a relation between the rod and the observer.

Until the observer is specified the length of the rod is quite-undeterminate." To axes on the earth the Michelson-Morley mirror system is not shortened, but to axes at rest relatively to the sun it is.

In 1905 Einstein also deduced a new principle of great importance from the theory of relativity, for he showed that as a necessary consequence of the new point of view concerning mass, velocity and time, a body which suffered any change in its energy content must simultaneously experience a change in its inertial mass. Mass and energy were thus shown to be identical concepts differing only in the units in which they are measured. Hence, merely in consequence of its mass a body has associated with it a specific energy compared with which the kinetic energy of its motion appears to be in general insignificant.

Changes in the energy content of bodies producing alteration in inertial mass and consequently in gravitational mass should therefore be accompanied by a change in weight. In the case of the combustion of oxygen and hydrogen the energy involved in the formation of water should produce a diminution in weight of the order of 1 in 300 millions, which is far beyond the accuracy of weighing at present attainable. In the case of the radioactive bodies the conditions are more favourable as with radium emanation a change of mass of about 1 in 20,000 should occur in four days, but the small quantity of emanation available does not render this method of verification at all possible.

The theoretical prediction of changes of mass in reacting systems resulting from the relativity principle is, of course, directly at variance with Lavoisier's generalisation of the conservation of mass. Whatever confirmation the future may bring of the predictions of theory, the principle of the conservation of mass stands at the moment as one of the most accurately verified generalisations of science.

The Special Theory of Relativity deals with the equivalence of reference systems either at rest or moving with uniform velocity relative to each other. The next obvious step was to extend, if possible, the relativity principle to all reference systems whatever their state of motion. Now it is found that a change of the reference system to one having accelerations introduces expressions for forces (such

as centrifugal forces) which are characteristic of the accelerated system chosen, and that consequently the general statements of phenomena are not capable of expression in an invariant form. This was the problem that Einstein then attempted to solve, and which he successfully accomplished and presented as the General Theory of Relativity.

To do this he introduced a physical hypothesis concerning gravitation as a result of considering the phenomena due to a gravitational field, which would be perceived by an observer in just the same way if he and his reference system moved with the same acceleration as was previously characteristic of the gravitational field at the point of observation. Gravitational problems were thus reduced to the general study of relative motion. "Furthermore," writes Einstein, "it was soon found possible to link up the science of gravitation with the special theory of relativity in a natural manner. In this connection I was struck by the fact that the force of gravitation possesses a fundamental property, which distinguishes it from electromagnetic forces. All bodies fall in a gravitational field with the same acceleration, or—what is only another formulation of the same fact—the gravitational and inertial masses of a body are numerically equal to each other. This numerical equality suggests identity of character. Can gravitation and inertia be identical? This question leads directly to the General Theory of Relativity. Is it not possible for me to regard the earth as free from rotation, if I conceive of the centrifugal force, which acts on all bodies at rest relatively to the earth, as being a 'real' field of gravitation, or part of such a field? If this idea can be carried out, then we shall have proved in very truth the identity of gravitation and inertia. For the same property which is regarded as *inertia* from the point of a system not taking part in the rotation can be considered as *gravitation* when considered with respect to a system that shares the rotation. According to Newton, this interpretation is impossible, because by Newton's law the centrifugal field cannot be regarded as being produced by matter, and because in Newton's theory there is no place for a 'real' field of the 'Koriolisfield' type."

This is embodied in what is called the Principle of Equivalence which, again quoting Eddington, may be stated as

follows: "A gravitational field of force is exactly equivalent to a field of force introduced by a transformation of the co-ordinates of reference, so that by no possible experiment can we distinguish between them." This statement, together with a four-dimensional geometry, necessitated by the Lorentz-Einstein transformation which showed that no event could be uniquely described except in terms of four co-ordinates x , y , z , and t , in which all four are inseparably associated, forms the basis of the General Theory.

As a result, the experimental fact that *all* bodies in the earth's gravitational field fall with *equal* acceleration becomes of prime importance in the new mechanics. The apparently strange numerical equality of gravitational and inertial masses which the experiments of Newton, Bessel (1784-1846) and Eötvös (1848-1919) based on the Galilei-Newtonian law of inertia, established as an empirical coincidence, is now seen to mean identity in character since they merely represent different aspects of the same phenomenon.

Einstein was thus led to the formation of a new system of mechanics which to the first order agreed with that of Newton. The agreement is extremely close, as the motions of the planetary bodies, with one exception, are accurately described in terms of the classical mechanics. It is at this point that the new mechanics is capable of being put to a crucial test. According to the Newtonian theory, in a system consisting of a single spherical sun and a single planet, the orbit of the latter will remain fixed with reference to the sun. If a second planet exists, however, its effect will be to cause the perihelion of the first to advance in the direction of rotation. In the case of our own system Mercury has long been known to be subject to an advance of its perihelion of 574 seconds per century, whereas calculation only accounted for 532 seconds, a discrepancy of 42 seconds. Astronomers have long sought some explanation of this phenomenon which, however, would be explicable if the sun's equatorial diameter exceeded its polar diameter by 0.5 second. This excess, however, has not been detected, nor has the relatively large effect it should have on the inclination of Mercury's orbit been observed.

Einstein, however, by calculation alone, using the results of the special theory of relativity (i.e. taking into account the variation of Mercury's mass with its velocity), and the

general theory of relativity (i.e. using a modified form of the law of gravitation) has accounted for the excess of 42 seconds within the limits of accuracy of the observations.

Einstein also proposed another crucial test which, as it involved the prediction of new phenomena, has shown that the theory possesses considerable heuristic value. Light is a form of energy, so Einstein claimed that it possessed mass, and in consequence of the general theory of relativity it should, therefore, suffer deflection in a gravitational field. Calculation showed that light passing close to the limb of the sun from a star, should be deflected by 1.75 seconds as distinct from 0.85 second as required by a corpuscular theory of light such as that of Newton. An opportunity of testing this remarkable prediction was provided by the total solar eclipse of 29 May, 1919, when the Royal Society and the Royal Astronomical Society equipped expeditions to Brazil and West Africa. Photographs of stars near the sun during the eclipse were compared with those of the same stars at a period when the sun was in another part of the sky, and the result was a striking confirmation of the theory.

A further conclusion from the theory that spectral lines issuing from the matter in the intense gravitational field of the sun should also show displacement towards the red end of the spectrum compared with similar lines from terrestrial sources has since been detected.

While the Relativity Theory has met with such conspicuous success in so many different branches of physics—in the motions of electrons, of planets, and of light—it promises to deal with many other problems of importance in connection with cosmogony, and has already attempted to answer such questions as the possibility of a "Finite" and yet "Unbounded" Universe, and the problem of the structure of space.

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CHAPTER XIV

THE QUANTUM THEORY

THE second of the clouds to which Kelvin referred in the quotation at the beginning of the previous chapter, that is, our difficulty regarding the Equipartition of Energy in the problem of Radiation, has been partly removed by Planck (b. 1858) whose papers on this subject date from 1900. As we have seen in a previous chapter (Chap. X) all attempts on the well-established principles of electrodynamics failed to give an expression for the energy of full radiation in accordance with facts.

The fundamental part of Planck's theory is that he denies altogether the equipartition theory. He considers a material enclosure containing radiation, and supposes that the material of the enclosure contains a system of fixed linear electric doublets or oscillators of the Hertzian type. The radiation in the enclosure passes over these now absorbed now radiated, and finally settles down in thermodynamic equilibrium with them.

By the application of the ordinary electro-dynamical principles he showed that in equilibrium the relation between the mean energy of an oscillator of frequency ν , (L_ν) and the energy density of the radiation of frequency ν , (U_ν) exchanging energy with it is given by—

$$U_\nu = \frac{8\pi\nu^2}{c^3} L_\nu.$$

It should be noted here that if L_ν is taken equal to kT (since there is potential as well as kinetic energy in an oscillator of the type considered) the Rayleigh-Jeans expression is obtained. Planck, to avoid this, then assumes that the absorption and radiation by the oscillators take

place in a discontinuous manner so that the energy of an oscillator at any instant must be an integral multiple of a unit or "quantum," which Planck assumes depends on the frequency, and is, in fact, proportional to it.

He then introduces the conception of thermodynamic probability into the kinetic theory, as was first indicated by Boltzmann in 1877, and briefly referred to in Chapter IX. From considerations of this nature he was able to calculate how the entropy of such a system depended on the temperature, and deduced that—

$$L_\nu = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \text{ whence } U_\nu = \frac{8\pi}{c^3} \frac{h\nu^3}{e^{\frac{h\nu}{kT}} - 1}.$$

Expressed in terms of wave-lengths this gives—

$$E_\lambda d\lambda = \frac{8\pi c^2 h}{\lambda^{-5}} \frac{1}{e^{\frac{ch}{\lambda kT}} - 1} d\lambda,$$

or as it is usually written—

$$E_\lambda d\lambda = C_1 \lambda^{-5} (e^{\frac{C_2}{\lambda T}} - 1)^{-1}$$

where C_1 and C_2 are constants.

Experiments by Lummer and Pringsheim in 1900, Paschen in 1901, and Coblentz in 1914, have shown that this formula gives a remarkable agreement with facts. In addition, it gives the displacement law of Wien, while the values of the various molecular constants, such as the Avogadro constant, the gas constant, and the unit of electricity deduced from it are in excellent agreement with directly determined values of these quantities.

For short wave-lengths Planck's formula assumes the form—

$$E_\lambda d\lambda = C_1 \lambda^{-5} e^{-\frac{C_2}{\lambda T}} d\lambda$$

and thus agrees with Wien's Law, while for long wave-lengths it reduces to

$$E_\lambda d\lambda = C_1/C_2 \lambda^{-4} T d\lambda$$

which is equivalent to the Rayleigh-Jeans Law.

With regard to the two constants h and k , Planck has pointed out that the ordinary C.G.S. units have an arbitrary foundation in the dimensions and motions of our planet, while "in contrast with this it might be of interest to note that, with the aid of the two constants h and k which appear in the universal law of radiation, we have the means of establishing units of length, mass, time and temperature, which are independent of special bodies or substances, which necessarily retain their significance for all times and for all environments, terrestrial and human or otherwise, and which may, therefore, be described as 'natural units.'

"The means of determining the four units of length, mass, time and temperature, are given by the two constants h and k mentioned, together with the magnitude of the velocity of propagation of light in a vacuum, c , and that of the constant of gravitation, f ."

We must now consider the "quantum" in more detail. Although on Planck's theory the interchange of energy between radiation and matter cannot take place continuously but only in jumps given by integral multiples of $h\nu$, the quantum is not a unit of energy, as its size depends on the frequency of the oscillation which is absorbing or radiating it. It is bigger for higher frequencies than for lower ones. Calculation shows that in the higher frequencies the quantum is very large compared with the average kinetic energy of the oscillators. For yellow light it is about sixteen times the average kinetic energy of an oscillator at a temperature of 1500°C .

It is thus easily seen that the energy distribution in the spectrum should present us with a maximum of energy at a certain wave-length falling off to vanishingly small amounts at longer and shorter wave-lengths, for in the short wave-lengths the "quantum" is very large, so that the probability that an oscillator possesses an amount of energy equal to it is smaller than at longer wave-lengths, while at the longest wave-lengths the quantum is so small that although a large number of oscillators may possess it, the total energy is still small.

Although Planck's theory showed itself capable of giving such a remarkable verification of the energy distribution in black body radiation, and allowed the determination of

important molecular constants with considerable accuracy, it did not receive a ready acceptance. The fundamental hypotheses were of a revolutionary character and, in addition, the deduction of the radiation formula was not entirely free from criticism, so that it was deemed desirable to consider all possible modes of escape from the difficulties which the new theory brought in its train before the theory could be given general recognition. The Equipartition Theorem had proved of great value, and it was difficult to see why it should give correct results in the case of long waves and not short ones. As Planck writes: "If the law of equipartition of energy held true in all cases, Rayleigh's law of radiation would, in consequence, hold for all wave-lengths and temperatures. But since this possibility is excluded by the measurements at hand, the only possible conclusion is that the law of the equipartition of energy, and with it the system of Hamilton's equations of motion, does not possess the importance attributed to it in classical dynamics. Therein lies the strongest proof of the necessity of a fundamental modification of the latter."

Although Planck's theory of the interchange of energy between radiation and matter was considered revolutionary, it was followed in 1905 by a still more radical conception which was introduced by Einstein to explain the photo-electric effect. Whereas Planck carefully limited the discontinuity to the actual mechanism of the energy exchange, Einstein assumed that even after energy were emitted according to the quantum principle in amount $h\nu$, the energy travelled through space in localised bundles or quanta. Some such theory involving the idea of a fibrous æther had already been proposed by J. J. Thomson, as we have seen in Chapter XII. At the time there was very little quantitative evidence available, yet Einstein predicted that the photo-electric effect would be in accordance with the relation

$$\frac{1}{2}mv^2 = h\nu - W,$$

in which $h\nu$ is the energy of the light absorbed by the electron, W the energy required to remove the electron from its atom and $\frac{1}{2}mv^2$ the kinetic energy of the ejected electron. From this equation it appeared that for the photo-electric effect to appear at all, the value of $h\nu$ must be greater than the energy W required to detach an electron,

and since h is a constant, the frequency of the light required to produce the photo-electric effect must be greater than a certain minimum value $\nu = W/h$, and that for frequencies greater than this the kinetic energy of the photo-electron varied linearly with the frequency.

The conception of the "unit of action" or "quantum," however, soon proved itself of signal service in other fields. Einstein in 1907 applied the idea to the consideration of specific heats with such success that the elucidation of the physical meaning of the quantum has become of paramount importance in the study of physics.

As long ago as 1819 Dulong and Petit had shown that the product of the specific heat and the atomic weights of many elements was a constant, having the value of 6 approximately. This result is known as Dulong and Petit's Law, and implies that the specific heats of atoms of all elements are the same. On the kinetic and equipartition theories, we have been led to attribute to each degree of freedom an amount of energy equal to $\frac{1}{2}RT$ if we consider a gramme atom. Hence the total energy of a gramme atom, including kinetic and potential energy, is $3RT$. The specific heat is simply the change in this for a change in temperature of 1°C. , so that the atomic heat should be equal to $3R$.

This result is in agreement with the experimentally deduced law of Dulong and Petit, and the work of other observers, who showed that at high temperatures many apparent exceptions obeyed the law. It should be mentioned that this agreement was considered one of the triumphs of the equipartition theory.

Besides this, the theory suggested that the specific heats should be independent of temperature as $3R$ is independent of T , but it is proved by the experiments of Nernst and others that the specific heat is a function of the temperature diminishing to extremely small values towards the absolute zero of temperature.

Einstein attacked the problem by assuming that in a monatomic solid the atoms have a definite frequency of vibration, and that the energy of the atoms is distributed among them, so that each has an integral number of quanta, each of which is $h\nu$ where ν is the frequency of the vibration, which he identifies with the residual rays or "rest-strahlen"

of Rubens. Thus if there are N atoms in a gramme atom the total energy is—

$$3N(L_\nu) = \frac{3N h\nu}{e^{kT} - 1}.$$

A differentiation of this with respect to T gives the specific heat which is of the form—

$$\frac{x^2 e^x}{(e^x - 1)^2} \text{ where } x = \frac{h\nu}{kT}.$$

If T is large this gives a constant for the specific heat in agreement with Dulong and Petit, while if T is small it tends to become zero. Einstein verified this equation in the case of the diamond, and found that it gave an excellent agreement, qualitative and quantitative, with experience.

Debye (b. 1884) also investigated this problem without assuming a characteristic frequency. From a knowledge of the elastic constants he has shown how the number of possible frequencies may be calculated in a manner similar to that of Rayleigh and Jeans in the case of the vibrations of an æther cube. The application of the quantum theory to these vibrations produced relations for the variation of the specific heat with temperature agreeing with the results of experiment extremely well.

The problem of the origin of the line spectra of gases has never yielded to treatment on the old classical mechanics, yet by a brilliant application of the quantum theory and the negation of certain results obtained by the old methods, Niels Bohr (b. 1885) in 1913 developed a theory of spectral lines which accounts, at any rate in the cases of hydrogen and helium, for the main series of lines in their spectra, and has predicted the existence of unknown series with remarkable accuracy. While Sommerfeld (b. 1868), by extending Bohr's treatment, and taking into account the results of the theory of relativity, has accounted for the fine structure of the individual lines in a surprising manner.

Bohr applied his conceptions to the atomic model deduced by Rutherford which is supported by considerable

experimental evidence derived from the study of the rays emitted by radioactive substances. On this theory the atom consists of a positively charged nucleus, round which are rotating electrons, the number of electrons being equal to the number of positive charges on the nucleus. Nearly all the mass of the atom is ascribed to the nucleus which is considerably smaller than the dimensions of the atom. Experiments on the scattering of α -rays show that the diameter of the nucleus is of the order 10^{-12} cm., while that of the atom is of the order 10^{-8} cm., so that an atom may be considered as resembling a miniature solar system.

Such an atom is dynamically unstable according to the classical electrodynamics, for on that basis the electrons must emit energy in rotating, and in consequence their orbits will shrink. Hence in a vacuum tube containing hydrogen atoms, there would be all possible sizes of orbits and hence all possible frequencies, so that the emitted radiation would be continuous in character and would not exhibit the discrete lines of the hydrogen spectrum. To avoid this difficulty Bohr makes use of two postulates to the effect that in rotating round a nucleus, the electron does not radiate energy, and that such rotation without radiation can only take place at certain distances from the nucleus, determined by a third postulate involving the quantum conception. These non-radiating orbits he refers to as "stationary" states.

Bohr restricted his calculations in the first place to circular orbits, and considered that in the stationary states the energy and velocities could be determined by the classical mechanics. He then defined the stationary states as orbits in which the angular momentum of the electron is an exact integral multiple of $h/2\pi$. These three postulates enable a visualisation of the atom to be obtained as a nucleus surrounded by electrons moving in discrete concentric orbits of radii proportional to the squares of successive whole numbers, that is, 1, 4, 9, 16, etc.

In order to account for the emission of radiation Bohr then introduces a Frequency Condition to the effect that when the electron passes from one stationary state characterised by energy W_2 to another stationary state in which the energy is W_1 , the amount of energy $W_2 - W_1$ is radiated

as a single energy quantum $h\nu$ of monochromatic radiation given by $W_2 - W_1 = h\nu$.

Now the assumption regarding the angular momentum is such as to make the values of the energies in the successive orbits inversely proportional to n^2 , where n is the number of the orbit, counting from the innermost one.

Hence the frequency of the radiation emitted by passage of an electron from orbit s to orbit t is proportional to $\left(\frac{1}{t^2} - \frac{1}{s^2}\right)$. This relation is immediately recognisable as of the general form expressing a series spectrum as discussed in Chapter X.

The actual expression obtained by Bohr in the case of the hydrogen atom in which the charges on the nucleus and the single rotating electron are equal to the unit charge e , is given by—

$$\nu = \frac{2\pi^2 me^4}{h^3} \left(\frac{1}{t^2} - \frac{1}{s^2} \right) = N \left(\frac{1}{t^2} - \frac{1}{s^2} \right).$$

If t is taken as 2 and s assumes the values 3, 4, 5, etc., the resulting values of ν gives the well-known Balmer series, while if we put $t = 1$ and give s the values 2, 3, 4, etc., a series in the ultra-violet is obtained which has since been discovered by Lyman (b. 1874).

Similarly the values $t = 3$, $s = 4, 5, 6$, etc., give the infra-red Bergman series the first two members of which were observed by Paschen in 1908 and the next three by Brackett in 1922.

Up to 1913 only twelve members of the Balmer series had been observed in laboratory experiments, although upwards of thirty have been detected in the spectra of certain nebulae. This is to be anticipated on Bohr's theory, for if the necessary calculations be made of the radii of the orbits corresponding to the Balmer series, it is found that the higher values of s necessitate orbits of the same order of magnitude as the mean free paths of the molecules of a gas. Thus $s = 14$ for the twelfth member gives a radius equal to the mean free path at about 7 mm. of mercury, so that to obtain these orbits a very low pressure is necessary, which in a vacuum tube would not involve a sufficiently large mass of gas to produce an observable effect. The

incandescent gas in certain nebulae does, however, provide a sufficient mass at low pressure for the production of the lines not observed in the laboratory. R. W. Wood (b. 1868) in 1920 succeeded in observing the Balmer series in the laboratory down to the twentieth member, and it was noticed that as the pressure was increased the higher members of the series successively disappeared as indicated by the theory.

The constant outside the bracket in the expression for ν is to be identified on Bohr's theory with the Rydberg constant, the importance of which we noted in a previous chapter. Its value calculated from the values of m , e and h is in close accord with the value obtained by experiment.

In the case of helium too, Bohr's theory met with great success in explaining its spectra. It is clear that an ionised helium atom which consists of a central nucleus of charge $2e$ with a revolving electron of charge $-e$ ought to have a similar spectrum to that of hydrogen. The appropriate substitution then shows that in this case the series spectrum is expressed by—

$$\nu = 4N\left(\frac{1}{t^2} - \frac{1}{s^2}\right).$$

The series given by $t = 1$, $s = 2, 3$, etc., is far in the ultra-violet and has not yet been discovered. Two members of that given by $t = 2$ were discovered by Lyman in 1919. The series given by $t = 3$ was discovered by Fowler (b. 1868) in 1912, but was attributed to hydrogen, while that given by $t = 4$ gives a series, alternate members of which coincide with the Balmer series for hydrogen, so that this spectrum can be emitted by both hydrogen and helium.

In this treatment it has been assumed that the mass of the electron is negligible in comparison with that of the nucleus. In actual fact the nucleus and electron will rotate round their common centre of gravity. By introducing this correction Bohr showed that the two Rydberg constants for helium and hydrogen should not be exactly as 4 to 1. From the actual measured values Fowler deduced for the ratio of the mass of the electron to that of the hydrogen nucleus the value 1 to 1836, which is extremely close to that obtained by Millikan (b. 1868) in a more direct way.

The theory is also in agreement with Einstein's work on the photo-electric effect, for in Bohr's theory ionisation is to be attributed to the expulsion of an electron from any orbit to an infinite distance, that is to say outside the atom. Now it can be shown that the kinetic energy of an electron in any stationary state is equal to the work required to remove the electron from the atomic system. Hence, if an amount of energy $h\nu$ is absorbed the kinetic energy of the ejected electron is given by $\frac{1}{2}mv^2 = h\nu - W$, where W is the energy in a stationary state. Now this is Einstein's equation, so that the Einstein photo-electric theory and the Bohr theory of spectra are both different aspects of the same phenomena.

Bohr's earlier work dealt only with circular orbits, which were completely specified by the angular velocity of the revolving electron, so that they had only one degree of freedom. Clearly under the electrostatic law of force which determines the motions in these orbits all types of Keplerian ellipses are possible. Now motion in an ellipse involves two degrees of freedom, so that if the quantum theory is to be applied to motion of this type, a new quantum condition must be introduced. This was successfully done in 1915 by Wilson and Sommerfeld, though the fruits of the work are to be ascribed almost solely to the latter.

Bohr had "quantised" the angular momentum of the electrons in their orbits. Sommerfeld in addition quantised the radial momentum in the orbits, which is equivalent to restricting the infinite number of elliptic orbits of the same stationary state to a number all having the same major axes but of definite eccentricity.

In place of the formula deduced by Bohr for the hydrogen series Sommerfeld obtained the general formula

$$\nu = N \left[\frac{1}{(t + t')^2} - \frac{1}{(s + s')^2} \right]$$

where t and t' are the two quantum numbers of the final orbit and s and s' those of the initial orbit. The Balmer series is given when $(t + t') = 2$ and $(s + s') = 3, 4, 5$, etc.

On this view then the number of orbits which can be

considered as taking part in the emission of the Balmer series is greatly increased, since corresponding to any total quantum number n there are n ways in which it may be divided between two subsidiary quantum numbers. Thus for the stationary state characterised by total quantum number 3 there will be orbits having the following azimuthal and radial quantum numbers (3, 0), (2, 1) and (1, 2), of which only (3, 0) is a circle.

The introduction of elliptic orbits having definite amounts of eccentricity presents the possibility of a phenomenon impossible under the original postulate of circular orbits. For with an eccentric orbit the electron will at some portion of its path be nearer to the nucleus than at others so that its velocity will vary. Since the velocities of the electron are not small compared with that of light, a variation of mass with velocity will occur, and the orbit will lose its closed character and exhibit an advancement of the perihelion similar to that exhibited by the planet Mercury and explained by Einstein by the theory of relativity. In consequence the energy in the various orbits corresponding to the same stationary state will depend on the eccentricity of the orbits, that is, on the individual values of s , s' , t and t' and not only on their sums $s + s'$ and $t + t'$. It follows, therefore, that transitions between stationary states no longer produce exactly the same line as given by Bohr's theory, but slightly different lines in addition.

In this way Sommerfeld explained the fine structure of the hydrogen and helium lines. The first member of the Balmer series should on this basis consist of five lines in two groups, the lines in one group referring to the final state in the two quantum orbits which is a circle and the other to the elliptic orbit. For certain reasons not all these lines are supposed capable of existence, but a constant doublet separation should be a feature of the whole Balmer series. This was accurately verified by Paschen in 1916 for the similar series in the ionised helium spectrum where the same theory applies, and by Shrum in 1923 for the first five members of the hydrogen series.

Bohr's theory has an immediate application to the theory of X-ray spectra. As we have seen in Chapter XII Moseley's work on the characteristic X-radiations emitted by the elements under the influence of electronic bombardment

showed that the frequency of the K and L radiations could be represented by the empirical relations—

$$\nu_K = R(N - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

$$\nu_L = R(N - 7.4)^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right)$$

where R is the Rydberg number and N the atomic number.

Thus the frequencies of these radiations depend on quantities of which only N depends on the particular element concerned, so that if the frequencies of the various K and L radiations are plotted against the atomic number of the element, i.e. against N, a regular shift in frequency is revealed. This regularity is strongly indicative that the origin of the X-ray spectra is very closely connected with the immediate neighbourhood of the nucleus of the atom, since it is here that changes in the nuclear charge will be most effective.

The relationships given above are very similar to the expressions for the first terms of the Lyman and Balmer series spectra for hydrogen so that it was reasonable to seek an explanation on the basis of the Bohr theory. This has been done by a number of observers, particularly Kossel (b. 1888) and Sommerfeld, with considerable success, so that in addition to a theory of optical spectra which have their origin on the external confines of the atom, there has been developed a very similar theory of X-ray series spectra dealing with the distribution of electrons in the innermost portions of the atom. According to this theory an atom of atomic number N consists of a nucleus having a positive charge of N units surrounded by N revolving electrons which are arranged in different rings. The innermost ring which will be a single quantum ring has been called the K ring, the next a two quantum ring has similarly been called the L ring and so on for the M and other rings. If the atom receives a sufficiently large stimulus one of the electrons from the K ring, for example, will be thrown outside the atom, that is the atom will be ionised from the inside and there will be a gap in the K ring. If now an electron falls from the L ring into this gap there will be emitted a radiation of frequency proportional to

$\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$, while if the gap is filled by an electron from the M ring the emitted frequency will be proportional to $\left(\frac{1}{1^2} - \frac{1}{3^2}\right)$. Similar considerations apply if the ejected electron was originally in the L ring when an electron from the M or other succeeding rings could fill the gap and so produce radiation of frequency proportional to

$$\left(\frac{1}{2^2} - \frac{1}{3^2}\right) \text{ or } \left(\frac{1}{2^2} - \frac{1}{4^2}\right), \text{ etc.}$$

In this way the K, L and M series of X-ray spectra have received an explanation in terms of Bohr's theory.

It will be noticed that in the above complete expressions for the first members of the K and L series, the nuclear charges were involved in terms of $(N - 1)^2$ and $(N - 7.4)^2$ respectively instead of N^2 . This is interpreted as a "nuclear defect" due to the screening effect of the electrons in the various rings, so that the electrostatic force on electrons in the neighbourhood of the nucleus is less than it would be if the nucleus alone were acting.

In spite of the great successes of the quantum theory before 1914 no definite experimental verification of the quantum relationship had been obtained. The existence of the quantum was of course quite definitely proven by the work of Planck, Einstein, Bohr and others, but only in an indirect manner, and in circumstances where the actual transference of energy from matter to radiation had not been subjected to measurement.

In 1914 Millikan gave definite and unambiguous proof of the exactness of the quantum relationship in the photo-electric effect as had been expressed by Einstein in 1905. By measuring the potential (V) necessary to prevent the emission of photo-electrons under the influence of light of given frequency he showed that

$$Ve = \frac{1}{2}mv^2 = h\nu - h\nu_0$$

where $h\nu_0$ is the work required to detach an electron and ν_0 the minimum frequency which would give the photo-electric effect at all. At the photo-electric threshold an amount of radiation $h\nu_0$ is just sufficient to remove an electron

from the metal, a less amount produces no effect, while with a greater quantity the excess goes to give kinetic energy to the electron. The value of h he deduced from these experiments was very close to that deduced by Planck from the experimental verification of the radiation laws.

While Millikan's experiments investigated the quantum relation involved in the transformation of energy from radiation to the kinetic energy of electrons, the reverse phenomenon received attention at the hands of a number of American investigators. Duane and Hunt in 1915 showed that when a target was bombarded with electrons of known velocity, as in a Coolidge X-ray tube, the maximum frequency of the general X-radiation emitted found to satisfy the relation

$$\frac{1}{2}mv^2 = h\nu.$$

The emission of the characteristic X-radiation has been also shown by Webster, Wagner and others to be in agreement with the quantum principle.

Similarly in the visible spectrum the work of Franck and Hertz in 1914 has shown the applicability of the theory to the collisions between atoms and electrons. These investigators showed that the collisions between electrons and mercury vapour atoms are perfectly elastic, so long as the energy of the electrons is less than that acquired in falling through a potential difference of 4.9 volts. When the electrons have this velocity or more the collisions become inelastic, and the electron either loses all its energy or the amount corresponding to 4.9 volts and at the same time the single line 2536 Å of mercury is emitted. This emission of radiation was found to be in accordance with quantum principles for the wave-length 2536 Å satisfies the relation $Ve = h\nu$ for $V = 4.86$ volts.

The explanation of this effect follows at once from the Bohr theory, for on this theory the absorption of energy corresponding to the first inelastic collision raises an outside electron in the normal atom to its second quantum orbit, so that the radiation emitted on the return of the electron will be the first member of an important series. As the energy of the electrons is increased an inelastic collision is to be expected each time the electron acquires energy

equal to $W_n - W_1$, where W_n is the energy in the n th orbit and W_1 that in the first or normal orbit. Finally, when the electrons have sufficient energy entirely to remove an electron from the atom, that is to ionise the atom, the shortest radiation emitted is that of the root or limit of the series. For mercury vapour the limit of the series of which the line 2536 Å. is the first member is 1188 Å. corresponding to an ionisation potential of 10.4 volts, which is in agreement with the measured value of this quantity.

While the quantum theory has presented us with a wonderful method of attacking many of the most intricate problems of radiation with a success which is truly amazing, it must at the same time be stated that it is completely unable at the present time to account for the phenomena of the interference, the diffraction and even the propagation of light. Planck, as we have stated previously, limited the occurrence of the quantum relation to the instants of emission and absorption of energy, though in his later treatment of the theory he has been able to discard it for absorption. Einstein, arguing very largely on the photo-electric effect and the analogous production of high speed β -particles by the absorption of X-rays, has presented us with a theory of light or radiation quanta in which radiation itself is supposed to have an atomic or quantum structure directly at variance with the conception of spreading waves essential for the interference and diffraction effects which the classical theory was so successful in explaining.

Physicists have in general completely accepted the quantum theory, but it is realised that the theory does not explain phenomena at all but merely allows us to describe them. Indeed, the conception has grown in many quarters, if we may quote Sir Ernest Rutherford who does not, however, identify himself with this view, that "it may be quite impossible in the nature of things to form that detailed picture in space and time of successive events that we have been accustomed to consider as so important a part of a complete theory. The atom is naturally the most fundamental structure presented to us. Its properties must explain the properties of all more complicated structures, including matter in bulk, but we may not, therefore, be justified in expecting that its processes can be explained in terms of concepts derived entirely

from a study of molar properties. The atomic processes involved may be so fundamental that a complete understanding may be denied us. It is early yet to be pessimistic on this problem, for we may hope that our difficulties may any day be resolved by further discoveries." Be that as it may the position is not of the happiest.

In this connection the attempts of Sir J. J. Thomson to avoid the difficulties of the quantum theory are of great interest. In 1924 he presented a theory of light in which he definitely assumed a dual structure of radiation, a continuous portion and a corpuscular portion of the Einstein type in which he visualised the quantum as a closed loop of electric force whose circumference is equal to the wavelength of light. This closed loop of electric force he assumed was propagated without change of form with the velocity of light in a direction at right-angles to its plane. For high frequencies most of the energy would be in the quantum and very little in the continuous waves, and *vice versa* for low frequencies. This type of theory also appeared to be a necessary consequence of intermittence in the action of electric force, the possibility of which was considered by Thomson in a paper on *The Intermittence of Electric Force* in 1925.

On this view the action of force consists in the production of finite increments of momentum after finite intervals of time, which vary at random instead of in the production of a continuous flow of momentum as expressed in Newton's Second Law. For events which take place in times long compared with the "time interval" of the force the new theory gives the same results as does the classical theory. On the other hand, for events taking place in periods short compared with the "time interval" of the force, such as occur in atomic systems, there exist definite probabilities whether or not the forces produce any effect, so that there is the possibility of phenomena not conceivable on the classical view-point. The probability of events of this type can be illustrated by reference to the effects of the alternation of an electric force of this description, for it is extremely unlikely that those electrons which in one application of the force chanced to receive movements of momentum will be those to receive the opposite increment on the reversal of the force. It is a consequence of the theory

that there would be no loss of energy by an electron rotating in a circular orbit. There would, however, be a radiation of energy which when it had spread out to a certain distance would be "reflected" back again, so that on the whole the energy would remain constant. Spontaneous transitions of the electron from one orbit to another would be possible also owing to the chance that the increments of momentum received during passage from perihelion to aphelion could be different from those received from aphelion to perihelion. The theory necessitates a corpuscular structure for light, and in addition requires accompanying Maxwellian waves. "I picture to myself," he writes, "the light unit as consisting of a central quantum vibrating with the period of the light and emitting electrical waves. These waves will not spread out from the quantum beyond a certain distance, which will be large compared with size of the quantum whose circumference is equal to the wave-length of the light, thus surrounding the quantum there will be a finite volume filled with electrical waves, but not allowing any to escape, and restoring to the quantum the energy it loses by radiation. On this view light has a dual character, consisting of electrical waves and the quantum; the electrical waves give rise to interference effects, the quantum to the photo-electric ones."

There is an obvious connection of some of the results of the theory with the failure of the old mechanics, particularly as regards the Bohr theory, the inexplicable numerical relationships and motions of which have led it to be described as a collection of rules. The further developments of this new aspect of the quantum theory will be awaited with great interest.

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CHAPTER XV

THE STRUCTURE OF THE ATOM

WE have seen in Chapters XII and XIV that the experiments and investigations of Rutherford, Soddy, Moseley and Bohr have led to the theory that an atom consists of an extremely small positively-charged nucleus surrounded by rings of electrons, and that the magnitude of the positive charge on the nucleus is given by the atomic number, and that this latter is the important feature of an atom and that on which its chemical and physical properties depend. Recent work has chiefly been concerned with the working out in more detail of this theory, and its support by very surprising evidence has enabled a considerable amount of certainty to be attached to the theory, and has at the same time enabled some remarkable deductions to be made on the constitution of matter in general.

The three main lines of investigation which we shall consider in this chapter are :—

- (1) The study of isotopes.
- (2) The constitution of nuclei.
- (3) The configuration of the electron rings.

The study of isotopes received a great impetus by the use of the positive ray analysis developed by Sir J. J. Thomson. The general principle of the method is very similar to that used in the determination of e/m for the cathode rays, in which the subjection of the rays to electric and magnetic fields results in their deflection by amounts depending on their velocity, mass and charge. Early results showed that in the case of mercury, for example, positively charged particles having from one to eight charges could be obtained. These correspond to the loss of from one to eight electrons from the electron system

which accompanies the positively-charged nucleus. Other interesting results showed the possibility of the existence, though doubtless transitory, of such unstable compounds as CH , CH_2 , and CH_3 . The most important result, however, was his discovery, in 1911, of the existence of two chemically identical forms of neon with atomic weights of 20 and 22.

This discovery extended the isotope principle from the radioactive elements, among which it was first discovered by Soddy and Fajans, and raised the question of how far other elements consisted of isotopes. In particular, the question of the non-integral value of the atomic weights which had troubled chemists in the time of Prout was revived with particular interest, as it was suggested that in these cases the non-integral value might be due to the co-existence in different proportions of isotopes of different atomic weights, even in the chemically pure elements.

Thomson's positive ray work was carried on by Aston (b. 1877) and others, and in consequence it has been shown that chlorine of atomic weight 35.5 consists of a mixture of isotopes of atomic weight 35 and 37 in the proportion of 3 to 1. This has been confirmed by Harkins, who managed by repeated diffusions to obtain samples of chlorine chemically identical but of different densities. A considerable number of the elements have now been found to consist of mixtures of isotopes; in the case of mercury as many as six were discovered, all of integral atomic weight varying from 197 to 204.

The case of the isotopes of rubidium and strontium is interesting, as they have isotopes of atomic weights 85.5 and 87, 85, 88, respectively, thus presenting an instance of isobares or elements with the same atomic weights. Their atomic charges are $37e$ and $38e$ respectively, so that the difference must be due to the presence of an extra electron in the nucleus of rubidium. This element, however, is known to be radioactive emitting slow β -particles so that it is not unlikely that in so doing it becomes strontium. Information respecting the isotopes of potassium which is also radioactive, and calcium, is not sufficiently definite to warrant a similar conclusion.

Since all the isotopes of an element have the same atomic number, we must conclude that the differences in the atomic

weights must be due to the addition of something to the nucleus which, as it does not alter the atomic number, must consist in part of negative electrons, thus showing that the nucleus is a very complicated structure. Since the atomic weights of the isotopes differ by as many as one, two, three, four and even more units, it is not inconsistent with the facts to assume that the nuclei of hydrogen and helium may account for the difference (the mass of the electrons being negligible), particularly as the nuclei of the radioactive elements are capable of ejecting helium nuclei and electrons, and the ordinary atomic weights of the elements show a very suggestive series of jumps of four units in many cases.

The general result of the study of isotopes leads to the conclusion that all nuclei are probably built up of electrons and nuclei of hydrogen and helium, while it is possible that the nucleus of the latter may itself consist of hydrogen nuclei, or protons, as they are called. The hydrogen nucleus thus takes the place of the "protyle" or hypothetical element which Prout tried to identify with the atom of hydrogen as the primordial stuff out of which all matter was built up.

Considerable experimental evidence has recently been obtained by Rutherford and his collaborators that this is the case. He has found that when swift α -particles pass through nitrogen a number of particles which he identified with hydrogen particles are produced as a result of the collisions. These particles in the most favourable case have velocities which give them a maximum range in air of 40 cm. The projection of α -particles into hydrogen never resulted in the production of particles of range greater than 29 cm., so that this greater range cannot be attributed to impurity in the nitrogen. Furthermore, no evidence of such H-particles, as they have been called, has been obtained in the case of oxygen or carbon dioxide.

Similar results were found in the case of aluminium, in which case the energy of the fastest H-particles produced was 40 per cent. greater than that of the α -particles producing them. This points to the conclusion that the source of some of the energy of these particles must be in the atoms from which they come—that they, in fact, explode under the influence of the α -ray bombardment and are

disintegrated. This result is extremely important, as it is the first occasion in which the intra-atomic energy has been artificially obtained, though as yet on an extremely small scale and only by the aid of a process which is at present beyond our control.

Although several elements have been shown capable of disruption under α -ray bombardment, it is a striking feature that in all cases their atomic weights have been capable of expression in the form $4n + 2$ or $4n + 3$, where n has had values from 1 to 7 suggesting that those of atomic weight $4n$, and consisting presumably of helium nuclei, are extremely stable.

Rutherford has made observations on the ranges of these particles which are expelled in all directions, and has found that the range in the direction of the α -particle is considerably greater than in the direction opposed to the α -particle, and has been enabled to suggest a nuclear structure in which protons are supposed to be not actually in the atomic nucleus but rotating very close to it, and in an extremely strong field of force.

The fact that the atomic mass of hydrogen is 1.008 on the scale which makes that of oxygen 16, and that of the isotopes of the elements integral numbers, calls for comment in considering the proton as an ultimate unit in the constitution of nuclei. We should expect that the atomic mass of helium would be 4.03 instead of 4.0 if the helium nucleus were constituted of four protons together with the two electrons of negligible mass which are necessary to reduce the nuclear charge to two units. The theory of relativity has indicated that there is a very close connection between mass and energy, so that it is possible to attribute the loss of mass in the formation of a helium nucleus to an evolution of energy which in some manner becomes available. Calculation of the amount of energy equivalent to the loss of mass shows that it is large even when compared with that given out in radioactive changes. It has even been suggested that the slow synthesis of helium from hydrogen on the sun and the stars would be capable of maintaining the existing rates of heat radiation for hundreds of millions of years.

The consideration of X-ray and optical spectra has thrown considerable light on the way in which the elec-

trons in an atom are distributed round the nucleus. The complete solution of the problem of the arrangement of the whole of the electrons is very difficult, as it is the solution of the n -body problem where n can be as high as 92. In the case of hydrogen in which there is a singly-charged nucleus surrounded by a single rotating electron Bohr's theory of its spectrum, together with Sommerfeld's extension to elliptical orbits, gives a complete spacial model of the hydrogen atom which is in agreement with a large number of facts. In the case of helium, the next simplest atom, difficulties have appeared which have prevented the deduction of a perfectly satisfactory model. It has been possible, however, by means of general considerations based on the information given by the periodic classification, chemical evidence with regard to valency and the theory of X-ray and optical spectra to deduce electron configurations which can be regarded as tentative solutions of the problem.

G. N. Lewis (b. 1875), in 1916, suggested a "cubical" atom based very largely on the chemical conception of valency. The theory is founded on the Rutherford conception of a nuclear atom surrounded by a number of electrons corresponding to the ordinal position of the atom in the periodic classification, and the assumption that groups of two or eight electrons form stable systems. This assumption was suggested by the remarkable chemical stability of the atoms of helium and neon containing 2 and $2 + 8$ electrons respectively. In the case of neon, the eight outer electrons are supposed to be arranged at the corners of a cube surrounding the nucleus, while for argon the eight additional electrons form another cube external to the neon cube. Chemical combination is supposed to be due to the tendencies of atoms to give up, or to receive electrons so as to resemble the inert elements. Thus, electropositive lithium, which contains one electron outside the helium pair tends to give up the extra electron, so that in the presence of electronegative fluorine with seven external electrons, an electron is transferred from the lithium to the fluorine resulting in the formation of Li^+F^- . Lewis also showed how the tendency to form completed systems of two or eight electrons could be accomplished by the sharing of one or more pairs of

electrons by two atoms. In this way he managed to obtain a very definite conception of a chemical bond as two electrons coupled together and held jointly by two atoms.

In 1919 and 1921 I. Langmuir (b. 1881) extended Lewis's theory, which dealt mainly with the elements of lower atomic number, to the whole of the periodic classification. His theory, like Lewis's, is based on the conception of completed electron systems which it is assumed are possessed by the inert elements in order to explain their great stability. The ordinal numbers of these elements are, helium 2, neon 10, argon 18, krypton 36, xenon 54 and radium emanation (niton) 86. Rydberg, in 1914, pointed out that these numbers can be obtained from the series

$$2 + 2 \cdot 2^2 + 2 \cdot 2^2 + 2 \cdot 3^2 + 2 \cdot 3^2 + 2 \cdot 4^2 + 2 \cdot 4^2$$

etc. This suggested that in addition to the stability inherent in systems of 2 and 8 (i.e. $2 \cdot 2^2$), systems containing 18 (i.e. $2 \cdot 3^2$) and 32 (i.e. $2 \cdot 4^2$) are similarly characterised by great stability. Langmuir therefore assumed that the outer electron shells of krypton and xenon each contained 18 electrons, while that of niton contained 32. The electrons in incomplete shells were postulated as valency electrons, chemical combination taking place through the tendency of the electron shells of two atoms to form completed shells by holding electrons in common. As there are only eight valencies Langmuir assumed a natural tendency of atoms to form shells of eight electrons, which he called "octets." On this assumption he then developed his octet theory of valency and managed to explain many of the characteristics of the elements and a number of the features of the periodic table where the existence of long periods and transition elements received more or less plausible explanation. The theory was rather artificial in many respects in spite of a number of successes which can be credited to it.

Bury, in 1921, succeeded in amending it, and was able to assign electron structures free from some of the objections which could be urged against Langmuir's theory.

He attributed the difficulties of Langmuir's theory to a too rigid adherence to the Rydberg numbers, and suggested that the maximum number of electrons in the outer shell (the valency electrons) was definitely eight, and that in

those cases where Langmuir had placed more than eight in an outer shell, the additional electrons should be put in an inner kernel shell which might have as many as eighteen or thirty-two electrons.

In 1921 also, Sir J. J. Thomson elaborated a theory of atomic structure and chemical combination which was largely based on his earlier theories of 1914, in which he first made use of the Rutherford atom and of 1906, in which he made use of his own conception of the atom—a sphere of positive electricity in which the electrons were embedded. In the latest form of his theory he used a variable law of force between electrons and nucleus in order to endow the various electron groups with the stability impossible in terms of the ordinary Coulomb Law. The law of force was given by

$$F = \frac{Ne^2}{r^2} \left(1 - \frac{c}{r}\right)$$

where F is the force on an electron in an atom of atomic number N at a distance r from the nucleus, and c is a constant of the order 10^{-8} cm., being the distance at which the attraction between nucleus and electron becomes converted into a repulsion. With this law of force successive shells of eight electrons arranged at the corners of a hypothetical cube round the nucleus can be stably arranged, and Thomson showed how ionisation potentials and elastic constants could be calculated, while many of the essentials of the “chemical” atom and the requirements of the periodic table could be successfully met by means of this atom.

The atom models of Lewis, Langmuir and Thomson are all “static” atoms, inasmuch as the electrons are arranged spacially in positions about which only small oscillations are possible. These models are not easily reconciled with the spectroscopic evidence. Indeed, it would be surprising if they were, for they all owe the genesis of their fundamental assumptions to purely chemical notions. The complete structure of the atom when known should enable the whole of the physical and chemical properties of the atom to be deduced from it, so that it is evident that the physical, and particularly the spectroscopic properties of

the atoms should enter very largely into any theory of atomic structure.

This physical aspect of the problem has been pressed into service by Bohr in his view of the electronic arrangement, and has formed the basis of his theory of Atomic Constitution published in 1921. This theory forms a logical extension of his theory of the hydrogen and helium spectra and of the X-ray spectra. Bohr attacked the problem by assuming a nucleus to be in some way stripped of its electrons and considered the reconstruction of the atom by successive "bindings" of single electrons in the various possible orbits. He divided the planetary electrons into groups according to the position of their orbits from the nucleus. The electrons in the innermost orbit—the K orbit—are characterised by a total quantum number of 1, those in the second orbit—the L orbit—by a total quantum number of 2, and so on up to orbits of quantum number 6. As in the other theories an outer group of 8 electrons forming a stable system is assumed to characterise the inert gases. Thus for the first element, hydrogen, there is a singly charged nucleus surrounded by a rotating electron which in the normal state is in the single quantum or K orbit. The second element, helium, has two electrons in a single quantum orbit. This group of two electrons in a single quantum orbit or K orbit is a common feature of all the elements except hydrogen. For lithium and the following elements successive electrons build up the second quantum orbit which is completed by neon with eight electrons. This completed two-quantum ring appears in all elements after neon. For the succeeding elements a third quantum ring is formed which is completed with eight electrons by argon.

After argon comes potassium, which starts a four-quantum orbit, then calcium with two electrons in the four-quantum orbit. With scandium the new electron goes into the three-quantum group, and we now get an inner ring changing and increasing the number of its electrons, so that by the time the first long period is completed with krypton there are 18 electrons in the three-quantum orbit and 8 in the four-quantum orbit. Similarly with xenon there are inner orbits having 2, 8, 18 and 18 electrons while the outermost orbit has 8 electrons, and for niton the numbers of the

electrons in the various orbits from the nucleus are, 2, 8, 18, 32, 18, 8, which are very similar to Bury's arrangement for these elements. So far, no complete mathematical exposition of the reasons underlying the choices in the various cases has been given, but general reasoning supported by a vast amount of relevant chemical and spectroscopic data at critical points has suggested the deduction of orbits for all the elements up to uranium. In particular all the problems of the periodic table, the long periods, the transition elements and the rare earths find natural explanation. The transition elements, it appears, are attributable to the development of the inner structure, while the outer ring of electrons containing the valency or "chemical" electrons remains practically unchanged.

So far nothing has been stated regarding the distribution of the various orbits. For the explanation of the hydrogen and helium spectra and of the X-ray spectra a co-planar arrangement of the orbits was assumed mainly for reasons of simplicity and as a first approximation to the actual configuration. Apparently for other than the spectroscopic phenomena some kind of spacial configuration is essential and Bohr has been led, in consequence, to assign to each electron an independent orbit in space. In a way the postulation of independent orbits is similar to the postulation of definite positions of the electron in the Lewis-Langmuir and Bury theories, so that the differences between the "static" atom and the "dynamic" atom of Bohr are, perhaps, not so irreconcilable as might at first appear.

In conclusion, quoting from Rutherford's Presidential Address to the British Association in 1923: "It may be of interest to try to visualise the conception of the atom we have so far reached by taking for illustration the heaviest atom, uranium. At the centre of the atom is a minute nucleus surrounded by a swirling group of 92 electrons, all in motion in definite orbits, and occupying, but by no means filling, a volume very large compared with that of the nucleus. Some of the electrons describe nearly circular orbits round the nucleus; others, orbits of a more elliptical shape whose axes rotate rapidly round the nucleus. The motion of the electrons in the different groups is not necessarily confined to a definite region of the atom, but

the electrons of one group may penetrate deeply into the region mainly occupied by another group, thus giving a type of inter-connection or coupling between the various groups. The maximum speed of any electron depends on the closeness of the approach to the nucleus, but the outermost electron will have a minimum speed of more than 1000 kilometres per second, while the innermost K electrons have an average speed of more than 150,000 kilometres per second, or half the speed of light. When we visualise the extraordinary complexity of the electronic system we may be surprised that it has been possible to find any order in the apparent medley of motions."

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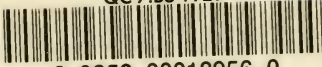
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